This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

LANE MEDICAL LIBRARY STANFORD
C81 .S85 1917 2 STOR
The elements of qualitative chemical ana
24503439839

LANE
MEDICAL LIBRARY
SEAL OF THE LELAND STANFORD JUNIOR UNIVERSITY
SEMPER VIRENS
1885
LEVI COOPER LANE FUND

THE ELEMENTS
OF
QUALITATIVE CHEMICAL ANALYSIS

WITH

SPECIAL CONSIDERATION OF THE APPLICATION OF
THE LAWS OF EQUILIBRIUM AND OF THE
MODERN THEORIES OF SOLUTION

BY

JULIUS STIEGLITZ
Professor of Chemistry in the University of Chicago

VOLUME II

PARTS III AND IV

LABORATORY MANUAL

LANE LIBRARY

NEW YORK
THE CENTURY CO.
1917

Copyright, 1911,
by
THE CENTURY CO.

Published, October, 1911
Reprinted, August, 1917

C01
S85
v.2
1917

PREFACE

THIS Laboratory Manual forms Parts III and IV of the author's "Qualitative Chemical Analysis." It is intended to be used in conjunction with Parts I and II, which are published as a separate volume and which contain the theoretical treatment of the subject. It will be sufficient to state here that Parts I and II include a discussion of the development and experimental foundations of the modern theories of solution; of the application of the laws of chemical and physical equilibrium to reactions used in analytical chemistry; of the theory of complex ions; of the electric theory of oxidation and reduction; and of the remaining important typical chemical actions used in analysis; all with special attention to substantiating the theoretical treatment by lecture experiments.

All of these topics are frequently referred to and intimately involved in the work of the laboratory course in qualitative analysis herewith presented.

The Laboratory Manual proper includes, as Part III of the author's book, a laboratory study of the analytical reactions of the common metal and acid ions and of the analysis of the various groups of these ions, as an introduction to the study and practice of systematic analysis. The laboratory work of this part (III) should be accompanied by classroom work on Part II of the first volume. The outline of systematic qualitative chemical analysis adopted forms Part IV of the book, and comprises the second half of the laboratory work provided for in this manual.

The author's viewpoint and the method of work recommended

44040

are fully discussed in the preface to the first volume of the work. Teachers interested are referred to that preface.

In the same place acknowledgment is rendered to authors whose works have been consulted, and to friends and colleagues, whose assistance has greatly helped the author.

JULIUS STIEGLITZ.

CHICAGO, *September*, 1911.

CONTENTS

PART III

STUDY OF REACTIONS

PAGE

A. REACTIONS OF THE METAL IONS:

The Alkali Group 3

The Alkaline Earth Group:

Equilibrium. Ionization Constants. Solubility-Product Constants. Relative Solubility 8

The Aluminium Group:

Amphoteric Hydroxides; Hydrolysis of Salts 22

The Zinc Group 30

The Silver and Copper Groups:

Complex Ions and Their Instability Constants 41

The Arsenic Group 52

B. REACTIONS OF THE ACID IONS:

Groups of Acids 65

The Group of Amphoteric Acids and Related Acids 67

The Carbonate Group 69

The Sulphate Group 71

The Chloride Group 72

The Phosphate Group 76

The Nitrate Group 79

The Group of Organic Acids 81

PART IV

SYSTEMATIC ANALYSIS

A. PRELIMINARY EXAMINATION 87

B. THE SOLUTION OF SUBSTANCES FOR THE SYSTEMATIC ANALYSIS FOR METAL IONS 94

PAGE

C. THE ANALYSIS FOR METAL IONS OF SUBSTANCES SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA......... 100
  The Precipitation and Analysis of the Silver Group............. 100
  The Precipitation of the Arsenic and Copper Groups........... 100
  The Separation of the Arsenic and Copper Groups............. 103
  The Analysis of the Copper Group.......................... 104
  The Analysis of the Arsenic Group.......................... 105
  The Zinc and Aluminium Groups............................ 107
  The Analysis of the Alkaline Earth Group.................... 114
  The Analysis of the Alkali Group........................... 114

D. THE ANALYSIS FOR THE ACID IONS OF SUBSTANCES SOLUBLE IN WATER, ACIDS, OR AQUA REGIA.......................... 115
  The Group of Amphoteric Acids and Related Acids............ 116
  The Carbonate Group.................................... 118
  The Preparation of a Solution for Examination for Acid Ions of the Sulphate, Chloride, Phosphate, and Organic Acid Groups.... 119
  The Sulphate and Chloride Groups.......................... 123
  The Phosphate Group.................................... 126
  The Nitrate Group...................................... 128
  The Group of Organic Acids............................... 129

E. THE ANALYSIS OF SUBSTANCES INSOLUBLE IN WATER, ACIDS, AND AQUA REGIA; THE ANALYSIS OF SILICATES................. 130
  Preliminary Examination.................................. 131
  Analysis.. 132
  The Analysis of Silicates................................ 134

APPENDIX

TABLE OF SOLUBILITIFS..................................... 140

TABLE OF EXACT SOLUBILITIES............................... 142

REAGENTS AND SOLUTIONS................................... 143

GENERAL LABORATORY INSTRUCTIONS

Apparatus. — 1. All apparatus must be cleaned and, when not in actual use, must be kept *clean* in the desk, ready for immediate employment. Distilled water is used for rinsing.

2. A *wash-bottle* and a set of *glass rods* (5, 7, and 9 inches long), rounded off at both ends, must be prepared.

Use of Reagents. — 1. Unless instructions call especially for the use of a *solid* reagent, the *solutions* of reagents on the desk-shelf and side-shelf are referred to in the instructions (but hydrogen sulphide is used as a gas, unless a solution of it is called for).

2. When instructions call for the use of the common acids and bases, without any specific qualification, the *dilute* solutions are intended to be used. *Concentrated* acids, etc., are used *only* when *specifically* called for.

3. The *concentrations* of all the reagents and solutions used are recorded in the table on pp. 143–147. In studying reactions, students should consult this table, so as to secure a basis for noting the intensity of reactions (precipitations, color reactions, etc.).

4. Reagents *must* be *filtered*, if they are not clear.

5. *Reactions* are tried, in test-tubes, with 5 to 6 c.c. of the solutions called for. A *small* excess of the reagent is used — that is, the reagent is added, until its obvious action (precipitation, solution, etc.) ceases. The common reagents represent rather strong solutions, and from 1 to 10 c.c. (usually 1 to 5 c.c.) of the reagent should be sufficient. An undue excess of reagents overloads solutions with matter foreign to the substance under examination and dilutes the latter.

Operations. — 1. Reactions are invariably carried out *at room temperature*, unless instructions specifically call for the application of heat. In the latter case the material under examination is *cooled for all operations subsequent to the one requiring heat*, unless specific instructions to the contrary are given.

2. *Filters* are used in funnels that are sufficiently large to leave at least a quarter of an inch of glass above the paper. A margin of more than one-half inch is avoided. The *size* of a *filter* is selected according to the *bulk* of the precipitate to be collected on it. *Traces* are collected on filters of 2 cm. diameter. The *centrifugal machine* is used with advantage in separating small precipitates from the great bulk of liquid, and the *filter-pump* is used for filtration.

3. All precipitates, which are collected on a filter, are *washed* twice, on the filter, with distilled water or with such reagent as the instructions call for.

Precautions. — 1. Potassium *cyanide* is a deadly poison. When it is used, special care must be taken to avoid breaking a glass vessel containing it, as the absorption of the poison by a cut would be extremely dangerous. When a cyanide solution is acidified, the operation must be carried out under a hood, to prevent the inhalation of hydrocyanic acid fumes.

2. **Concentrated sulphuric acid** and concentrated nitric acid must be handled with great care. Concentrated sulphuric acid is *added to* water, alcohol, solutions, etc., very slowly and with constant cooling of the vessel used.

3. **Solid oxidizing agents** — nitrates, chlorates, permanganates, dichromates — must be used in small quantities, and care must be taken not to heat, or rub in a mortar, any mixture of such an agent with a strong reducing agent (organic substances, cyanides, ferrocyanides, ferricyanides, sulphides). When the analytical work demands the destruction of such a reducing agent (*e. g.* organic matter) by a powerful oxidizing agent, the laboratory instructions contain specific directions as to the process to be used.

Records. — 1. In the *study* of *reactions*, all *observations* should be *recorded* at once, briefly but accurately, on the blank leaves provided for that purpose. Since the laboratory instructions are largely put in the form of questions, the record of observations is necessary to make the text complete and to render it available in connection with the later work on systematic analysis. Answers to questions of theory, equations, etc., should be given in a separate notebook. The formulæ for common substances will be found in the lists of reagents, pp. 143–149.

2. The form of *record* to be kept in *systematic analysis* is given on p. 88. Blank sheets for the records may be secured at the storeroom. All observations should be noted down *at once*. Particular attention must be paid to recording whether the presence of a trace or of a large or small quantity of a component is indicated.

LABORATORY MANUAL

PART III

STUDY OF REACTIONS

A. REACTIONS OF THE METAL IONS

THE ALKALI GROUP

Potassium-ion, K^+, *Sodium-ion*, Na^+, and *Ammonium-ion*, (NH_4^+)

1. Test aqueous solutions of each of the following compounds with neutral (violet) litmus paper, comparing the tints with that of a piece of the paper put into pure water:

(*a*) Potassium hydroxide, sodium hydroxide and ammonium hydroxide; test also the vapor above the solutions. Interpret the results.

(*b*) Sodium chloride, ammonium chloride, potassium sulphate, potassium carbonate.

2. (*a*) Slake some calcium oxide, in a small beaker, by adding a little water to it, then add a few cubic centimeters of ammonium chloride solution, and place a watch crystal over the beaker with moist pieces of neutral and red litmus paper sticking to the lower side of the crystal. Judging by 1 (*a*), would potassium and sodium salts react in the same way as ammonium chloride?

(*b*) Repeat the test in 2 (*a*), using limewater in place of slaked lime. Compare (*a*) and (*b*). Which gives the better result? Which will give a more concentrated solution of ammonium hydroxide? Express by the equilibrium law, applied to the dissociation of ammonium hydroxide into ammonia and water, how the concentration of the first will affect the test.

3. Heat a little of each of the following solid salts, in a porcelain dish or crucible, with the free flame, but below red heat: potassium, sodium and ammonium chlorides; sodium-ammonium-hydrogen phosphate. Observe which salts are volatile. If any fumes are given off, test them with moistened neutral litmus paper.

4. (*a*) Add one drop of a 10% solution of chloroplatinic acid, H_2PtCl_6, to one drop, each, of molar solutions of the chlorides of potassium, sodium and ammonium.

(*b*) Repeat the tests, but first dilute 0.1 c.c. of each of the solutions with 10 c.c. of water, and add one or two drops of the chloroplatinic acid solution to each of the diluted solutions. Allow these to stand ten or fifteen minutes and then evaporate them to dryness in porcelain dishes over a water bath; add two or three *drops* of cold water to the contents of each dish.

Can we distinguish potassium from sodium salts by this test? potassium from ammonium salts? According to (*b*), what are the necessary conditions for applying this test successfully?

5. Dilute 0.1 c.c. of the molar solutions of potassium chloride and ammonium chloride to 10 c.c. each.

(*a*) Add to 5 c.c. of each of the undiluted and the diluted solutions two drops of sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, solution.

(*b*) To the remaining 5 c.c. of the diluted solutions add 5 c.c. of the sodium cobaltinitrite solution.

Allow the mixtures to stand for fifteen minutes. The precipitates have the composition $K_2Na[Co(NO_2)_6]$, H_2O, and $(NH_4)_2Na[Co(NO_2)_6]$, H_2O. Explain the effectiveness of the large excess of reagent shown in (*b*). Which is the less soluble precipitate?

A solution, in which this test for potassium-ion is to be made, must be neutral or slightly acid, and, if alkaline, should be made slightly acid, with acetic acid, before the solution of $Na_3[Co(NO_2)_6]$ is added to it. Ammonium salts are first removed by ignition (§ 3).

6. Add 2 c.c. of potassium pyroantimonate $K_2H_2Sb_2O_7$ solution to two drops each of solutions of the chlorides of potassium, sodium and ammonium; shake the mixtures and scratch the sides of the test-tubes with glass rods, then let the mixtures stand thirty minutes. Note the *crystalline character* of the precipitate, $Na_2H_2Sb_2O_7$, 6 H_2O, as an essential characteristic of the salt. A solution, in which this test for sodium-ion is to be made, must be neutral or slightly *alkaline;* if it is acid, it should be made alkaline with potassium hydroxide solution, before the pyroantimonate is added to it.

7. Heat a little of the following salts, on the end of a clean (test?) platinum wire, in the nonluminous flame, and observe the flames with the naked eye and through a thick piece of cobalt glass:

(*a*) The chlorides of potassium, sodium, ammonium, each separately. Clean the wire until it gives no color to the flame, allow it to cool, touch it with the fingers and heat it again in the flame. What difference is there between the behavior of this minute trace of sodium chloride and that of the larger quantity of sodium chloride?

(*b*) An intimate mixture (*e.g.* the mixed solutions) of approximately equal parts of potassium chloride and sodium chloride.

(*c*) (*a*) and (*b*) may be repeated, the flames being examined with the aid of the spectroscope; the position of the main lines observed should be noted down. Consult the instructor.

8. Using the results obtained in 1 to 7, devise a scheme of analysis for detecting potassium, sodium and ammonium salts in the presence of one another, without the use of the spectroscope. Show the scheme to the instructor and ask for an "unknown."

Characteristic of the alkali metal ions is that all their common salts are easily soluble in water. The hydroxides of sodium and potassium are very strong bases, the hydroxide of ammonium a weaker one, but still moderately strong.

The Spectroscope.[1] — The prism spectroscope, in which the spectrum is produced by the unequal refraction of light of different wave lengths, is a convenient one to use for the purposes of qualitative analysis. The most common form consists of a prism, a telescope tube called the collimator, through which the light from the object examined is admitted, an observing telescope through which the light is examined, and a third short telescope containing a scale. The collimator has, at one end, an arrangement for admitting light through a narrow slit, with an adjustment to make the slit narrower or wider. At the other end of the collimator there is a lens. When the slit is brought into the focus of this lens, the rays of light from the slit leave the lens and pass to the prism as parallel rays. The receiving telescope collects these parallel rays and produces an image of the slit. If the source of light emits rays of different wave lengths, these will be unequally refracted in the prism and distinct images of the slit will be seen in the receiving telescope, in positions corresponding to each of the wave lengths.[1] If the source of light is white light, a *continuous spectrum*, consisting of images produced by waves of continuously increasing lengths, will be seen. If the source of light sends out only light of definite wave lengths, a *line spectrum* is seen, the lines being distinct images of the slit, in positions corresponding to the wave lengths of the light emitted. Thus potassium light shows, besides other fainter lines, two bright *lines*, a *red* one (corresponding to the wave length,[2] 768 $\mu\mu$) and a *violet* one (corresponding to the wave length 404 $\mu\mu$).

---

[1] Landauer's *Spectrum Analysis*, translated by Tingle (1907), and Vogel's *Qualitative Spectralanalyse* (1889) are recommended for reference.

For the observation of spectra the instrument is adjusted as follows: the *observing telescope* is unscrewed from the stand, to which it is attached, and is carefully focused on some distant object. It is then screwed into position again, and the *slit* of the *collimator* brought into the focus of the lens of the collimator in the following way: A Bunsen flame, in which sodium light is produced by a loopful of sodium chloride or sodium carbonate on a platinum wire or by the tip of a glass rod, is placed before the slit, four or five inches from it and in line with the collimator tube. The receiving telescope is then turned until the yellow line of sodium vapor is seen in the telescope; the line may appear blurred. If such is the case, the adjustable tube, holding the slit in the collimator, is moved forward or backward until the sodium line appears *sharply defined*. The slit is then in the focus of the collimator lens. Finally, one adjusts the *scale* in the third, short telescope, which is so set, that light, passing from it to the prism, is *reflected* directly into the receiving telescope in the path of the rays from the slit. The scale enables one to determine, fairly accurately, the position of lines in the spectrum. It is, frequently, a miniature photograph of an ordinary millimeter scale, showing regular intervals between the lines. Modern instruments may also be obtained, in which the scale is divided according to *wave lengths*, so that the latter may be used directly for the identification of lines. A scale reading from 400 $\mu\mu$ to 800 $\mu\mu$ is sufficient for ordinary purposes. The scale is brought into proper position as follows: a small luminous Bunsen flame or a tiny electric light is placed in front of the scale and the adjustable tube containing the scale is moved back and forth in the telescope tube until the scale is seen *sharply defined* in the receiving telescope. Sodium light is then observed against the scale, and if the *fixed side*[3] of the sodium line does not coincide with the scale line showing the wave length[4] 589, the telescope containing the

---

[1] Where the wave lengths are very nearly the same, a small instrument may not be able to separate the corresponding images.

[2] The wave lengths are given in terms of 1/millionth of a millimeter, which is designated by the symbol $\mu\mu$. The values given in the text are taken from Landauer-Tingle's *Spectrum Analysis*, where the lengths are given in terms of 0.1 $\mu\mu$. The red potassium line may be seen, in a good instrument, as consisting of two lines (of wave length 769.9 and 766.5 $\mu\mu$).

[3] The slit is made narrower, or wider, by changing the position of one of its sides, the other side is fixed, and adjustments to a scale are based on this fixed side, which appears fixed also in all the images of the slit.

[4] The wave length corresponding to the main sodium double line.

scale is carefully turned, until the adjustment indicated is shown. It is best to have the scale tube fastened down when the adjustment has once been made. For the observation of lines, especially of fainter ones, care must be taken to keep the illumination of the scale as reduced as is consistent with reading.

If a reduced millimeter scale is used in an instrument, the scale is placed so that the sodium line lies on some definite position on the scale, a little to the left of its center. On some scales this position may be marked 50, on others 100 and on others 0. For instance, for a scale reading from 0, at the red end of the spectrum, to 250 at the violet end, the correct position for the sodium line is 100. The reduction of wave lengths to readings on a scale with equal divisions (*e.g.* a reduced millimeter scale), and conversely, the reduction of readings on such a scale to wave lengths is most easily carried out, with sufficient accuracy for qualitative purposes, with the aid of a curve plotted on coördinate paper: wave lengths of known lines are plotted as ordinates and the corresponding positions of the lines on the scale of a given instrument are determined by experiment and plotted as abscissæ of the curve. The following lines are recommended for the purpose, the numbers representing wave lengths expressed in $\mu\mu$: K, 768 (red line); Li, 671; Cd, 644 (red line, spark spectrum; see p. 12); Zn, 636 (red line, spark spectrum); Na, 589; Tl, 535; Mg, 518 (spark spectrum); Cd, 509 (green line, spark spectrum); Sr, 461 (blue line); K, 404 (violet line).

By the combination of prisms of different kinds of glass (crown and flint glass) *direct-vision spectroscopes* have been constructed, in which the source of light, the prisms and the observing telescope are in a straight line. Direct-vision spectroscopes have also been constructed on a miniature scale, of a size which makes it convenient to carry an instrument in the pocket. Such *pocket spectroscopes* may also be used in qualitative analysis. The dispersion is smaller and the position of the lines is read with somewhat greater difficulty, than is the case, when the older type of instrument is used.

For the **observation of a flame spectrum** the spectroscope is adjusted in the manner described above, a nonluminous Bunsen flame, about four inches long, is brought in front of the slit (about six inches distant from it) and adjusted so that the *inner blue cone* of the flame is sufficiently lower than the slit to be altogether *out of the range of vision;* otherwise lines, or bands of lines, of the *carbon spectrum* of the blue cone would be seen, which could easily be mistaken for lines of other elements. The material to be examined, *e.g.* KCl, is then introduced into the flame in a loop of platinum wire; if the wire is fastened in a small piece of glass tubing, the latter may be conveniently slipped over the metal arm of a small stand. The observations are best made in a darkened room, and *the greatest cleanliness in regard to wires, vessels, etc., must be observed, on account of the delicacy and sensitiveness* of most spectroscopic tests.

The use of **electric spark spectra** in qualitative analysis will be described on p. 12, the use of **absorption spectra** on p. 24.

THE ALKALINE EARTH GROUP

Barium-ion, Ba^{++}, *Strontium-ion*, Sr^{++}, *Calcium-ion*, Ca^{++}, *Magnesium-ion*, Mg^{++}

(*Equilibrium. Ionization Constants. Solubility-Product Constants. Relative Solubility.*)

1. (*a*) Add a little water to some magnesium oxide or hydroxide and test the liquid over it with litmus paper.

(*b*) Shake some magnesium oxide with a little water and observe whether much of it dissolves. Add, to a part of the mixture, some hydrochloric or nitric acid (a slight effervescence would be due to the presence of a little magnesium carbonate in the oxide). What is formed? Give the equation. Oxides of what class combine readily with acids?

(*c*) Add some sodium hydroxide to another part of the mixture of solid magnesium oxide and water. Is there any perceptible change? What does the result show as to acid properties of magnesium hydroxide?

The hydroxides of barium, strontium and calcium show the same typical behavior as magnesium hydroxide towards hydrochloric acid and sodium hydroxide. See the table at the end of Part IV as to the relative solubilities of the hydroxides in water.

2. Test aqueous solutions of barium chloride and magnesium sulphate with neutral litmus.

3. Add to magnesium chloride solution some ammonium chloride, a little ammonium hydroxide, and then some ammonium phosphate added drop by drop. The precipitate is the *double* salt, magnesium-ammonium phosphate, $Mg(NH_4)PO_4,6\,H_2O$, which is used as a *characteristic test* to identify magnesium-ion after the removal of all other metal ions, excepting those of the alkalies.

4. (*a*) Add to some *concentrated* barium chloride solution an equal volume of *concentrated* sodium hydroxide solution (10 molar), which should be as free as possible from carbonate (side-shelf). Note the crystalline appearance of the precipitated barium hydroxide.

(*b*) Add to another portion of the barium chloride some *concentrated* ammonium hydroxide solution (15 molar; free from carbonate). (Note: on standing in the air, carbon dioxide is absorbed and

traces of barium carbonate are formed *from the surface downwards.*)

(*c*) To another portion of the barium chloride add some of the sodium hydroxide solution *diluted* with twenty-five parts of water.

(Traces of a *flocculent* precipitate are barium carbonate or silicate, due to slight impurities in the alkaline solution.)

Taking (*a*), (*b*) and (*c*) together, is ammonium hydroxide as active or strong a base as sodium hydroxide?

5. (*a*) Mix 5 c.c. of magnesium chloride solution with 10 c.c. of water and with ammonium hydroxide (the ordinary reagent, not the concentrated solution) as long as it will give a precipitate. Comparing 4 (*b*) and this result, which is less soluble in water, magnesium or barium hydroxide?

(*b*) Filter the solution from the magnesium hydroxide precipitated in (*a*), and add ammonium phosphate to the filtrate. Did the ammonium hydroxide precipitate the magnesium-ion completely?

(*c*) Add to 5 c.c. of magnesium chloride solution 10 c.c. of ammonium chloride and then ammonium hydroxide. Is a precipitate formed? To understand this result carry out 6, 7, 8.

6. To 100 c.c. of water add a few drops of phenolphthaleïn, and put about 10 c.c. of the mixture into each of six test-tubes. To the first and second add a *drop* of sodium hydroxide. The resulting change in color is a characteristic test for hydroxide-ion (for bases), just as is the litmus paper test — but phenolphthaleïn is not as *sensitive* a test for hydroxide-ion as is litmus (table, Chap. V). Add to the deep red solution in the second test-tube a few crystals of sodium chloride and shake the mixture. Is there any marked change in color? To each of the other four tubes add a *drop* of ammonium hydroxide, and then add to the red liquid in one of the four, drop by drop, one or two cubic centimeters of ammonium chloride solution, which should be tested with litmus to ascertain that it has no decided acid reaction. What does the gradual change in color show in regard to the concentration and activity of the hydroxide-ion? When the solution has finally become colorless, test it with litmus to ascertain whether it is alkaline at all, or whether the hydroxide-ion has too small a concentration to affect phenolphthaleïn.

To one of the other test-tube solutions reddened by a drop of ammonium hydroxide, add solid ammonium nitrate or sulphate, to another, sodium chloride. What conclusions may you draw as to the effect of a neutral *ammonium salt* on the strength of ammonium hydroxide as a base, or on its power to form hydroxide-ion? This is typical for the action of neutral salts of any *weak* base on the free base itself. Neutral salts of a weak acid have a similar effect on the acidity of the free weak acid itself (Chap. VI).

7. (*a*) Give the chemical and the mathematical equations for the equilibrium between ammonium hydroxide and its ions. [The decomposition of ammonium hydroxide into ammonia and water may be ignored. The resulting equation shows the true *efficiency* of the solutions as solutions of a base (see Chap. IX).] In a solution containing 3.5 g. ammonium hydroxide (0.1 mole) per liter, conductivity measurements show that 1.31% is ionized and 98.7% is nonionized.[1] What, then, are the concentrations of the ammonium-ion and the hydroxide-ion and of the nonionized substance? Substitute these values in your equilibrium equation and calculate the ionization constant for ammonium hydroxide. In a solution containing 0.35 g. of ammonium hydroxide per liter, 4.07% is ionized and 95.9% nonionized. What are the concentrations of the ammonium-ion and the hydroxide-ion and of the nonionized substance in this solution? Calculate the constant from these data also.

(*b*) In a solution of 5.35 g. of ammonium chloride (0.1 mole) per liter, about 85% of the salt is ionized. What change, then, would ammonium chloride produce, if 5.35 g. were added to the solution containing 0.1 mole of ammonium hydroxide per liter, as given in (*a*)? What would the total concentration of the ammonium-ion now be? Why would equilibrium not be possible without further change? Calculate what the approximate concentration of the hydroxide-ion must be in this mixture, when equilibrium is reëstablished.

(*c*) Why does sodium chloride not have the same decided effect on sodium hydroxide?

8. (*a*) Give the equation for the "solubility-product" or "ion-product" constant for magnesium hydroxide in its saturated solutions, *i.e.* for solutions in a condition of equilibrium with the solid hydroxide. A liter of water at 18° dissolves 0.009 g. magnesium hydroxide; its molecular weight is 58; express this

---

[1] A. A. Noyes, *Carnegie Institution Publication*, No. 63, p. 177 (1907)

concentration of 0.009 g. per liter in parts of a mole per liter. Considering the hydroxide to be *practically completely ionized*, what is the concentration of the magnesium-ion? of the hydroxide-ion? Substitute these values in the solubility-product equation and calculate the solubility-product constant for the saturated solution.

(*b*) What should happen if some barium hydroxide solution is added to the saturated magnesium hydroxide solution, increasing the concentration of the hydroxide-ion? Test your conclusion by adding a few cubic centimeters of concentrated barium hydroxide solution to 20 c.c. of a saturated, clear solution of magnesium hydroxide.

(*c*) In a 0.5 molar solution of ammonium hydroxide 0.57% is ionized[1] and the concentration of hydroxide-ion is 0.00285; in a 0.1 molar solution of magnesium sulphate 37% of the salt is ionized. What then would be the value of the solubility-product for magnesium hydroxide in a mixture containing 0.5 molar ammonium hydroxide and 0.1 molar $MgSO_4$? Judged by the solubility-product constant (§ 8 (*a*)) would magnesium hydroxide be precipitated from such a mixture? Test your conclusion by adding 5 c.c. of 0.2 molar magnesium sulphate solution to 5 c.c. of molar ammonium hydroxide.[2]

The influence of the ammonium sulphate, which is formed in the action, is in the same direction as that shown by ammonium chloride in the experiment studied below in (*d*). After carrying out (*d*), state whether a *complete* precipitation of magnesium hydroxide is to be expected under the conditions given in this paragraph (*c*); (see also § 5 (*b*) above).

(*d*) If to 0.5 molar ammonium hydroxide sufficient ammonium chloride is added to make the concentration of ammonium-ion 0.46, what concentration of hydroxide-ion would the mixture contain (consult § 7 (*b*))? What value, consequently, would the solubility-product have in a mixture containing 0.5 molar ammonium hydroxide, sufficient ammonium chloride to make $[NH_4^+] = 0.46$, and 0.1 molar magnesium sulphate? Judging by the value of the solubility-product constant, should we expect magnesium hydroxide to be precipitated under these conditions? Test your conclusion by adding[1] 0.32 g. of NH_4Cl to the mixture obtained in (*c*) or by adding 0.32 g. of NH_4Cl to 5 c.c. of 0.2 molar $MgSO_4$ and mixing the resulting solution with 5 c.c. of molar ammonium hydroxide.[2]

---

[1] Kohlrausch and Holborn, *Leitvermögen der Elektrolyte* (1898), p. 160.

[2] The solution should be free from ammonium carbonate.

9. (*a*) To 5 c.c. of manganous chloride solution add a few drops of ammonium hydroxide solution; to another 5 c.c. add a few cubic centimeters of ammonium chloride solution and then sufficient ammonium hydroxide to render the mixture alkaline (litmus). Zinc, nickelous, cobaltous, ferrous salts and salts of certain other bivalent metal ions behave in the same way.

(*b*) Carry out the same tests as in (*a*) with ferric chloride solution. Aluminium and chromium salts behave in the same way.

According to these results, which hydroxides are more insoluble in water — those of (*a*) or of (*b*)? If in doubt, add some ferric chloride to the mixture obtained in (*a*). The difference is sometimes used for a separation or recognition of the two groups (see Chap. X).

10. Magnesium salts do not color the Bunsen flame. The temperature of the electric spark is very much higher and with its aid we can obtain the most sensitive and reliable qualitative test for magnesium, its spectrum showing, with a very narrow slit of the spectroscope, a very characteristic double line[3] in the green part of the spectrum; the double line becomes a single line if the slit of the spectroscope is widened a very little. 0.0001 milligram of magnesium in a drop of liquid can be detected in this way. The test is a convenient one for confirming the presence of magnesium salts (Instructor).

Spark Spectra.[4] — A convenient way of making spectroscopic tests of solutions with the electric spark is the following: a piece of glass tubing, of about 5 mm. internal diameter, is drawn out to a capillary, the capillary is cut off close to the tube, and a short piece of fine platinum wire (1 to 2 cm.

---

[1] 0.32 g. NH_4Cl in 10 c.c. represents a concentration of 32 g. or $32/53.5 = 0.6$ mole per liter. The salt is ionized about 77% in the mixture. The slight increase in volume produced by the addition of the salt may be ignored here.

[2] The solution should be free from ammonium carbonate.

[3] With a very sensitive instrument, the double line may be resolved into a group of three lines. The wave lengths of the two brightest lines are 518 and 517 $\mu\mu$.

[4] *Cf.* Vogel's *Spectralanalyse*, p. 96, or Landauer-Tingle's *Spectrum Analysis*, p. 54.

long) is inserted through the narrow opening of the tube in such a way that 2 to 3 mm. of the wire protrudes into the tube and the remainder is left outside (see the "cup" in Fig. 1). The wire is then sealed into the tube, before a blowpipe, and the glass tube cut off about 5 mm. above the point where the wire is fused into it; the edges of the cup are rounded in a flame. This little cup[1] may be placed on one end of a small V tube, made of glass tubing slightly narrower than that used for the cup, and filled with mercury. The platinum wire of the cup should be in contact with the mercury, which is connected at the other end of the V tube with a wire leading to the *negative* terminal of a Ruhmkorff coil[2] capable of producing a spark 1 to 2 inches long. One or two *drops* of the solution under examination are put into the cup and a short piece of capillary tubing, 0.5 to 1 mm. wide, is inserted in the cup over the point of the platinum wire (see the figure). The capillary should be long enough to reach 1 or 2 mm. above the edge of the cup; in this position it lifts

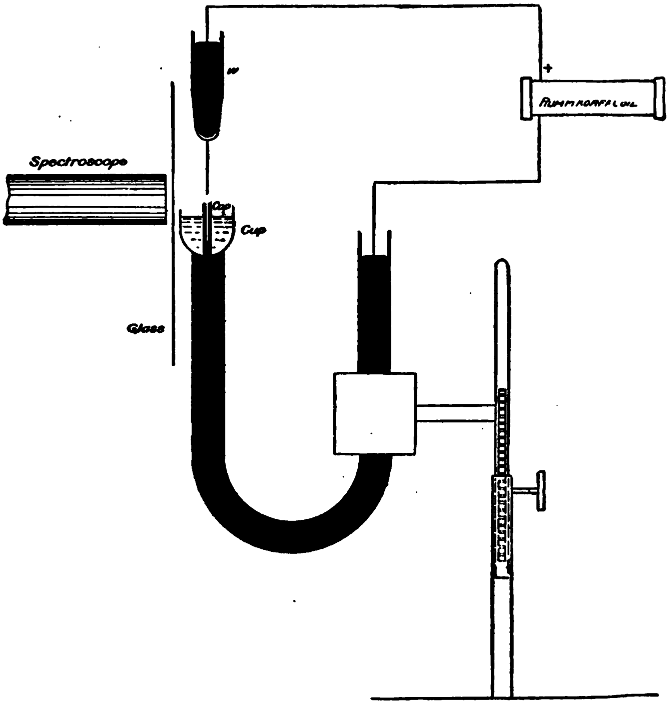


Fig. 1.

---

[1] A supply of these cups is kept ready for immediate use.

[2] Two or three large storage cells are used to supply the current; no condenser is required.

the liquid to a point just above the level of the cup. The point of a platinum wire, connected with the positive terminal[1] of the Ruhmkorff, is placed above the end of the capillary and within 1 or 2 mm. of it. When the spark is allowed to pass, some of the liquid is carried into the spark gap and the metal vapor formed in the spark may easily be examined with the aid of the spectroscope. The slit of the spectroscope is brought close to the spark, and is protected against the spattering droplets and acid fumes by means of a shield of very thin clear glass, placed between the spark and the instrument. For the detection of the faintest *traces* of magnesium and similar metals, it is better to use a cup of the same shape as the one described, but the platinum wire is made to pass through the cup to about 1 mm. above its edge; a capillary is used as before and is slipped over the platinum wire and should end evenly with it. With such faint traces the lines will often not be continuously seen, but will flash out occasionally with great brilliancy, and they may then be readily identified by their position.[2]

Most of the metal ions produce line spectra, when solutions of their salts (especially of the chlorides) are examined with the aid of the spark, and some of the spectra, like that of iron, contain a very large number of lines. Consequently, when this method of identification of an element is used, care must be taken to make exact readings of lines and to base a decision on the observation of a group of characteristic lines, rather than on that of a single line, whenever the element in question produces a spectrum, which should show several lines. In the most important work, the identification is frequently based on a direct comparison of the spectrum under observation, with that of any element whose presence is suspected: light obtained from the element in question is reflected, by means of a device attached to the slit of a spectroscope, into the upper half of the slit, and the light from the solution under examination is limited to the other half: in the case of identity, the lines observed in the upper and lower halves of the field will coincide.

In the test for magnesium, as for all metals, *scrupulous cleanness* of apparatus, cups, wires, capillaries, etc., must be observed and pure reagents must be used. The cups and wires are cleaned by means of repeated treatment with hydrochloric acid. It is best to make a blank test with the cup, etc., before the solution, that is to be tested, is placed in the cup.

---

[1] The correct adjustment may be readily recognized by a pale blue light which appears at the point of the negative wire in the spark gap.

[2] The passage of the spark through the air produces an *air spectrum;* the air spectrum, when the spark is passed in the direction given, is faint and does not interfere with observations of metal lines, if care is taken to keep the cup full enough of liquid to supply the capillary and the spark with an excess of electrolyte. With *very dilute* solutions, the air lines become more prominent, but, with practice, they may be easily discounted, being continuously present, while the metal lines, in such cases, flash up brilliantly at intervals. The presence of an ample amount of liquid in the point of the capillary also prevents the spark from attacking the glass and forming calcium vapor, etc.

11. Test a little of each of the chlorides of the other alkaline earths in the flame, on a clean platinum wire.[1] The flame colorations may be examined with the spectroscope and the most characteristic lines noted.[2]

12. (*a*) To a few cubic centimeters each of solutions of barium, strontium, calcium and magnesium chlorides, kept separate, add an equal amount of water and a few drops of dilute sulphuric acid. Observe sharply any difference in the speed with which a precipitate may form in the different cases.

(*b*) To a few cubic centimeters each of solutions of barium, strontium and calcium chlorides, kept separate, add dilute sulphuric acid until no more precipitate is formed in each case. Filter the solutions and add to each of the filtrates three volumes of alcohol. What do the results show in regard to the relative solubilities of the sulphates in water? (They are insoluble in alcohol.)

(*c*) Mix a *drop* of each of the chloride solutions with about 10 c.c. water and add a drop or two of dilute sulphuric acid. From your observations decide again the relative solubilities in water of the sulphates.

(*d*) To a solution of barium chloride add, in separate tests,

(1) Some saturated solution of strontium sulphate.

(2) Some saturated solution of calcium sulphate.

Then add the same reagents to strontium chloride and to calcium chloride. What do these results show as to the relative solubilities of the sulphates?

(*e*) Mix 5 c.c. each of molar solutions of barium chloride and calcium chloride in a beaker, add an equal volume of water, heat the mixture to boiling, and, stirring it vigorously, add, drop by drop, 5 c.c. of 0.5 molar sulphuric acid, prepared from one volume dilute acid and five volumes of water. Cool the mixture, centrifuge it (if possible), decant the solution and collect the precipitate on a very small filter, wash the filter and precipitate with

---

[1] The wire is kept clean by keeping it in hydrochloric acid, or heating it with the acid, rinsing it with water and heating it in the flame; if it still colors the flame, the treatment is repeated.

[2] Barium chloride gives a more characteristic line spectrum if a loopful of ammonium chloride is held in the flame under the barium salt; the hydrochloric acid, formed by the decomposition of the ammonium chloride, reduces the amount of decomposition of the barium chloride in the flame; Vogel, p. 154.

tium or calcium oxalate from a solution of the sulphates? Test such of your conclusions as seem doubtful.

Calculate the solubility-product constants for $BaSO_4$ and $SrSO_4$, using the table. What is the limit for the ratio of concentrations of the barium and strontium ions, required for the precipitation of barium sulphate before strontium sulphate?

Characteristics of the Group of Alkaline Earth Metal Ions. They form strong bases, which are more or less soluble in water and are not precipitated by ammonium hydroxide in the presence of ammonium chloride (difference from the aluminium group). Their sulphides are not precipitated from an aqueous solution (difference from the zinc, copper, silver and arsenic groups). Their carbonates (excepting magnesium carbonate) and phosphates (including magnesium phosphate) are very insoluble in water and are easily precipitated (difference from the alkali group).

Analysis of the Alkaline Earth Group

There are various combinations of the reactions of the alkaline earth metal ions, which may be used for a scheme of analysis of the group. Ask for an unknown and analyze it according to one of the two following methods.

METHOD A[1]

I. *Precipitation of Barium, Strontium and Calcium Carbonates. Detection of Magnesium and of Traces of Barium and Calcium.*

1. Add to the solution 10 to 15 c.c. of ammonium chloride, sufficient ammonium hydroxide to make the reaction alkaline, and ammonium carbonate until no further precipitate is produced, when ammonium carbonate is added to a little of a filtered sample of the liquid, or to the clear supernatant liquid, formed when the precipitate is allowed to settle. Heat the mixture gently and then collect any precipitated carbonates of **barium, strontium** and **calcium** (P) on a filter, using the filter pump to hasten the filtration (Instructor). In the filtrate (F), we may have traces of barium, strontium and calcium and all of the **magnesium.** Add a

---

[1] Fresenius, *Qualitative Analysis* (1909), p. 159

drop or two of dilute sulphuric acid to a small portion of the filtrate and observe whether a slight precipitate is formed in the course of a few minutes. (Very slight fine precipitates are often overlooked, without experience. Consult the instructor as to the best method for seeing one.) If a precipitate is formed, it can only be **barium** sulphate.

Add to another portion of the filtrate (F) some ammonium oxalate. A slight precipitate would most likely be **calcium oxalate**, especially if it is formed in a few minutes; on prolonged standing, difficultly soluble double oxalates of magnesium and ammonium are liable to be precipitated. If considerable magnesium is found (see below), the presence of calcium in this precipitate may be confirmed by allowing the precipitate to settle, decanting the liquid, washing the precipitate once by the same method, dissolving it in a drop of hydrochloric acid and a few drops of water and adding a drop of dilute sulphuric acid, and then four volumes of alcohol to the clear or filtered solution (see p. 15, § 12 *b*). Alcohol would precipitate **calcium** sulphate. The possible trace of strontium in the filtrate (F) is neglected.

2. The filtrate (F) having been tested for traces of barium and calcium, any such traces are removed from the main portion of (F) by means of a drop of dilute sulphuric acid and some ammonium oxalate, and the filtrate from the precipitated traces is tested for magnesium by means of ammonium phosphate. If no precipitate is formed, endeavor to start crystallization by frequent vigorous shaking of the mixture. A *crystalline* precipitate would show the presence of **magnesium**. A *flocculent* precipitate may be *aluminium* phosphate. Such a precipitate is allowed to settle, the liquid decanted and the precipitate treated with acetic acid; magnesium-ammonium phosphate is dissolved, aluminium phosphate is not. The acetic acid solution is filtered from any residue and neutralized with ammonia; a crystalline precipitate is **magnesium**-ammonium phosphate. (*Vide* p. 12, in regard to the spectroscopic test for magnesium.)

N.B. — If the filtrate (F) should have been allowed to stand overnight before it is tested, *magnesium*-ammonium carbonate, $(NH_4)_2Mg(CO_3)_2,4H_2O$, is liable to crystallize out; any crystals are dissolved in acid and ammonium hydroxide and ammonium phosphate are added to the solution.

II. *Separation and Detection of Calcium*

1. The precipitated carbonates (**P**) (**barium, strontium** and **calcium** may be present as carbonates) are placed in a porcelain dish and treated with dilute nitric acid, added, drop by drop, as long as there is any effervescence. The contents of the dish are evaporated to dryness and the apparently dry nitrates heated in the dish on a wire gauze over a small flame, until no moisture collects in a cold beaker held for a moment over the dish. *Shut off the flame,* pulverize the nitrates as soon and as rapidly as possible, add 5 to 10 c.c. of an anhydrous ether-alcohol mixture (care! inflammable!), mix the liquid and solid thoroughly and filter the solution through a very small filter moistened with ether-alcohol, and wash the residue with a little more of the ether-alcohol mixture. The solution (**S**) contains any **calcium** nitrate, the residue (**R**) the nitrates of **barium** and **strontium**. *Any moisture present or allowed to be absorbed* will make strontium nitrate somewhat soluble and will vitiate the result.

2. To the solution (**S**) add a few drops of dilute sulphuric acid, bring any precipitated calcium sulphate on a small filter, wash it with alcohol, dissolve it in water, and add some ammonium oxalate to the solution to confirm **calcium**. If traces of strontium are to be looked for in (**S**), in very exact work, consult Fresenius, pp. 160–161.

III. *Separation and Detection of Barium and Strontium*

1. Dissolve the residue (**R**) in about 50 c.c. of water, add 3 or 4 drops of acetic acid to the solution, heat it to boiling and slowly add potassium chromate to the boiling liquid until the solution is deeply colored. A precipitate would be **barium** chromate. After removing the solution by filtration, confirm the presence of **barium** by dissolving the precipitate in very little dilute hydrochloric acid and water and testing the solution first with the flame (green **barium** flame) and then with sulphuric acid (white precipitate of **barium** sulphate).

2. To the filtrate from the barium chromate, ammonium hydroxide and ammonium carbonate are added and the mixture is warmed. If a precipitate is formed, it is most likely **strontium**

carbonate, but may be calcium carbonate. Collect it on a filter, wash it, moisten it with hydrochloric acid and make the flame test for **strontium.** In case of doubt, match the color with that of strontium chloride.

METHOD B[1]

I. *Precipitation of Barium, Strontium, Calcium and Magnesium Carbonates*

Add to the solution (which is concentrated, if necessary, to about 10 c.c.) 30 c.c. of a mixture of ammonium carbonate[2] and ammonium hydroxide and then add 30 c.c. 95% alcohol. Allow the mixture to stand for at least half an hour, shaking it frequently. Collect the precipitate on a filter, wash it with a little of the ammonium carbonate mixture, using the filter pump to hasten the filtration (Instructor). The precipitate contains all of the **barium, strontium** and **calcium,** as carbonates, and the **magnesium,** as $MgCO_3,(NH_4)_2CO_3, 4H_2O$.

II. *Separation and Determination of Barium*

The precipitated carbonates are dissolved in hot acetic acid (10 to 25 c.c.), which is poured gradually through the filter. The solution is first rendered slightly alkaline with ammonium hydroxide (litmus test) and then made just acid to litmus by means of acetic acid, added drop by drop to the solution; finally an excess of 2.5 c.c. of the acid is added. The solution, diluted to 40 c.c., is heated to boiling and 10 c.c. of a molar solution of K_2CrO_4 is added, a few drops at a time, to the boiling liquid. Finally the mixture is kept near the boiling-point for one or two minutes. The solution is filtered, even if it appears clear, and any precipitate, $BaCrO_4$, is washed thoroughly with cold water, after the filtrate (F) has been removed. Confirm the presence of **barium** by dissolving the precipitate in very little dilute hydrochloric acid and testing the solution with the flame.

---

[1] Bray, *J. Am. Chem. Soc.*, **31**, 615 (1909).

[2] Side-shelf reagent: 100 g. of powdered ammonium carbonate is dissolved in 300 c.c. of NH_4OH (sp. gr. 0.96). If the liquid is not clear, it is filtered; 100 c.c. of NH_4OH (sp. gr. 0.90) is added to the solution.

III. *Separation and Determination of Strontium*

The filtrate (F) may contain **strontium, calcium** and **magnesium.** It is cooled and concentrated ammonium hydroxide is added to it until the color changes from orange to yellow, and then an excess of 3 c.c. is added. The solution is diluted to 60 c.c. and 50 c.c. of 95% alcohol is slowly added to it. A pale yellow precipitate, $SrCrO_4$, shows the presence of **strontium.** Collect the precipitate on a filter over the filter pump, but do not wash it. The filtrate (FF) is reserved for examination for calcium and magnesium. To confirm the presence of **strontium,** transfer the precipitate, with the filter if necessary, to a porcelain dish, cover it with 35 c.c. of a mixture[1] of sodium oxalate, sodium carbonate and potassium chromate and boil the mixture gently for 3 to 5 minutes, the dish being covered with a watch glass. The precipitate is collected on a filter, washed thoroughly with water and treated with 5 c.c. of 5% acetic acid, the solution being poured repeatedly through the filter. A yellow precipitate, remaining on the filter, would be barium chromate, a white precipitate would be calcium oxalate. The filtrate, containing strontium acetate, is made alkaline by an excess of ammonium hydroxide and treated with 3 to 5 c.c. of ammonium carbonate mixture, heated to boiling, and set aside for a few minutes. A white precipitate confirms the presence of **strontium.** A flame test, which is compared with that of strontium chloride, may be made.

IV. *Separation and Determination of Calcium*

The filtrate (FF) (Sect. III) is treated with 5 c.c. of potassium chromate solution and 10 c.c. of alcohol, to remove the last traces of strontium and barium, if much of these has been found. If a precipitate forms, it is collected on a filter and the filtrate examined for **calcium** and **magnesium.** It is diluted with water to about 200 c.c. and treated with an excess of ammonium oxalate solution, the oxalate being added slowly to the boiling, stirred liquid. A precipitate, CaC_2O_4, would indicate the presence of **calcium.** The precipitate is collected on a filter and the filtrate (FFF) reserved for examination for the presence of **magnesium.** To confirm the presence of **calcium,** dissolve the precipitate, or a portion of it, in 5 c.c. cold dilute sulphuric acid and add 10 to 15 c.c. 95% alcohol to the solution obtained; alcohol would precipitate $CaSO_4$, if present.

---

[1] Side-shelf reagent, containing 30 g of $Na_2C_2O_4$, 6 g. of Na_2CO_3, and 3 g. of K_2CrO_4 per liter.

V. *Determination of Magnesium*

The filtrate (**FFF**) from the calcium oxalate is still to be tested for **magnesium:** it is cooled and treated with an excess of concentrated ammonia (10 c.c.) and with 20 c.c. of sodium phosphate solution. If no precipitate is formed, the mixture is shaken and allowed to stand for half an hour, with frequent shaking of the liquid. A white *crystalline precipitate,* $MgNH_4PO_4,6\ H_2O$, shows the presence of **magnesium.** A flocculent, noncrystalline precipitate is examined further according to § 2, p. 18.

THE ALUMINIUM GROUP

Aluminium, Chromium, Ferric Iron

Aluminium-ion, Al^{+++}, and *Aluminate-ion,* AlO_2^-

(Amphoteric Hydroxides; Hydrolysis of Salts)

1. Add sodium hydroxide, drop by drop, to two portions of a solution of aluminium sulphate, until a heavy precipitate of aluminium hydroxide is formed in each.

(*a*) To the one precipitate add hydrochloric acid in excess. What is formed? What property of aluminium hydroxide is shown here? What ions does it form which give it this property? Give the equations.

(*b*) To the other precipitate add more sodium hydroxide, in excess. What property of aluminium hydroxide is shown here? What ions does it form which give it this property? What compound is formed in the solutions? Give the equations.

(*c*) Write the chemical and mathematical equilibrium equations, in general terms, for an aqueous solution of aluminium hydroxide (it is not absolutely insoluble), and its ions, for both forms of ionization. Show the effect of an addition of hydrochloric acid on *each* condition of equilibrium. Then show, likewise, the effect of an addition of sodium hydroxide on *each* condition of equilibrium.

2. Test a solution of aluminium chloride, nitrate or sulphate, with neutral litmus paper. Does the result show that aluminium hydroxide is a strong or a weak base (Chap. X)?

Sodium and potassium aluminate solutions react strongly alkaline. What does this fact prove as to the strength of aluminium hydroxide as an acid?

3. Add ammonium hydroxide, in moderate excess, to a solution of aluminium sulphate. Is aluminium hydroxide readily soluble in excess of ammonium hydroxide? Compare the result with that obtained in 1 (*b*) and explain the difference.

4. (*a*) Add sodium hydroxide gradually, in moderate excess, to a solution of an aluminium salt and use the clear solution of sodium aluminate for the following experiments:

(*b*) Add ammonium hydroxide to a portion. Compare the result with 3 and explain the difference.

(*c*) Add hydrochloric acid very gradually, to another portion, until the solution is acid, and then add ammonium hydroxide in excess. Record all your observations, explain the reactions, and give the equations.

5. Add ammonium sulphide to a solution of an aluminium salt. Collect the precipitate on a filter, wash it and the filter four or five times with water, and then dissolve the precipitate in hydrochloric acid. Is a gas (odor) evolved? Is the precipitate a sulphide? Explain the result.

6. (*a*) Repeat 5, using sodium or ammonium carbonate in place of ammonium sulphide. Is the precipitate $Al_2(CO_3)_3$? Explain as before.

(*b*) Add to aluminium nitrate or chloride an excess of well-shaken milk of barium carbonate (side shelf); close the test-tube with the thumb and shake it carefully. When, after the addition of a little more barium carbonate, no more gas is given off on shaking the tube, filter the solution from the precipitate.

(*c*) Transfer the precipitate to a porcelain dish, add a gram or two of solid barium hydroxide, the same amount of anhydrous sodium carbonate, and 20 c.c. of water; boil the mixture, and filter the hot solution. Acidify the filtrate with hydrochloric acid, boil it and add to the solution just enough ammonium hydroxide to change the color of red litmus paper, and then one or two drops excess, and boil the mixture again. Observe whether a flocculent precipitate is formed. *This is a final test, used in identifying aluminium.* The reactions involved are the same as in 4 (*a*) and (*c*). Barium hydroxide and sodium carbonate, which form sodium hydroxide, are used in place of purchased sodium hydroxide, because this almost invariably contains alumina or silicic acid. The latter gives the same test with ammonium hydroxide as do aluminium salts.

7. Add a trace of cobalt nitrate to a crystal of aluminium sulphate or nitrate in the cavity of a piece of charcoal and ignite the mixture with a blowpipe (Instructor). The resulting blue compound (cobalt aluminate) is confirmative, but not conclusive, evidence of the presence of aluminium. There are some other blue cobalt salts which resist the action of heat — especially phosphates and silicates — and give a somewhat similar test.

8. Aluminium salts give no very characteristic flame or electric spark spectrum. But, even in traces, they affect the color of logwood extract in a characteristic fashion, and aluminium can be identified by a study of the change of color, that is, the change of the *absorption of light*, by means of the spectroscope. (See Vogel's *Spectralanalyse*, p. 202.) The test is particularly valuable because it can be made in the presence of many organic compounds, which interfere with the ordinary tests for aluminium (see Part IV). Prepare a logwood decoction, by boiling a chip with 20 c.c. of water in a perfectly clean test-tube. Dilute the solution with boiled, distilled water, until the absorption band next to the sodium line appears in the spectroscope as a *separate band* (Instructor), then add 1 c.c. of a solution of alum, containing 1 milligram of aluminium, and note the change of the absorption.[1]

Absorption Spectra. — Observations of the absorption spectra of substances form one of the most valuable methods of spectroscopic analysis. In the study of colored organic and inorganic bodies its application is indispensable. For the examination of an absorption spectrum for ordinary analytical purposes, the slit of the spectroscope is illuminated with *white light:* direct sunlight, the light from an Argand burner, an electric lamp or similar source of artificial light may be used. The solution under observation is best examined in a glass vessel with plane parallel walls, but an ordinary, large test-tube may be used, if care is taken to bring the tube close to the slit, in such a way that the light passes through the middle of the tube into the slit. Vapors

---

[1] Consult Vogel, *loc. cit.*, in regard to the application of this test in the presence of iron and of organic substances.

of metals absorb light of the same wave length as they emit and such absorption spectra are frequently *line spectra,* consisting of *dark lines* visible against a bright background (the dark, or Fraunhofer, lines in the spectrum of the sun result from such absorption). Colored solutions, glasses, etc., usually show *absorption bands* rather than sharply defined absorption lines. The position of such bands is determined by reading, on the scale, the point of maximum absorption and the points where a band begins and ends. The width and intensity of the bands depend on the concentration of the solution, but, usually, there is no difficulty in finding, by proper dilution, the concentration showing a *characteristic* absorption.

Chromium-ion, Cr^{+++}, *and Chromite-ion,*[1] CrO_2^-

1. Chromium forms two common oxides, — chromic oxide, Cr_2O_3, and chromic acid anhydride, CrO_3. What is the valence of chromium in each? The hydroxide of the lower oxide is amphoteric, but chiefly a base, like aluminium hydroxide; the hydroxides of the higher oxide are acids. Salts of chromic oxide are green or violet, salts of chromic acid are yellow or red.

What kind of reaction would be used to convert a salt of chromic oxide into a chromate? for the reverse process?

(*a*) Fuse any chromium salt with some sodium carbonate and potassium chlorate, on a crucible lid, and extract the cooled mass with water. What is the rôle of the chlorate in the fusion? of the sodium carbonate? Add lead acetate and acetic acid to the aqueous extract. The yellow precipitate is lead chromate, $PbCrO_4$. This is a *specific test* to *identify chromium.*

(*b*) Treat a little of a solution of a chromium salt with sufficient sodium carbonate to produce a precipitate ($Cr(OH)_3$) and then add a *little* sodium peroxide (care!) and warm the mixture. Na_2CrO_4 is formed. This is another *specific identification test* for *chromium.*

(*c*) Acidify a few cubic centimeters of potassium chromate solution and pass hydrogen sulphide in *excess* into the solution. Filter the solution. What does the change of color from orange to green indicate? (Do not write the equation for the action until Chap. XV on *oxidation* and *reduction* has been studied.)

2. Use a solution of chromium chloride or sulphate for the same tests as given under 1 (*a*) and (*b*) for aluminium. After using the excess of sodium hydroxide according to 1 (*b*), heat the

---

[1] *Chromate-ion,* $CrO_4^{=}$, is studied among the acid ions, *q. v.*

solution obtained to boiling. A partially dehydrated, difficultly soluble variety of chromium hydroxide is precipitated. How does this affect the hydrolysis of sodium chromite? What difference from aluminium is shown here? Can aluminium be separated from chromium by this means?

3. The reactions described for aluminium under 2, 5, 6 (*a*) and (*b*), but not 6 (*c*), are also shown by chromium. These facts should be noted, but the experiments need not be made.

4. Heat some sodium-ammonium-hydrogen phosphate (microcosmic salt) on the end of a platinum wire, add a minute fragment of a chromium compound to the clear bead and heat the mixture in the flame.

Chemistry of the Metaphosphate Bead. — When *microcosmic* salt, *sodium-ammonium phosphate*, $NaNH_4HPO_4, 4H_2O$, is heated, it first loses its water of crystallization and ammonia, decomposing, like all ammonium salts (Chap. IX), into ammonia and the acid of the ammonium salt, which, in this case, is sodium-dihydrogen phosphate: $Na(NH_4)HPO_4 \rightarrow NH_3 \uparrow + NaH_2PO_4$. The sodium-dihydrogen phosphate loses water and forms a clear bead of sodium metaphosphate: $NaH_2PO_4 \rightarrow H_2O \uparrow + NaPO_3$. The last action is *reversible*. For instance, when the metaphosphate is heated with water, it slowly combines with the latter and again forms sodium-dihydrogen phosphate. Besides being capable of combining with water (hydrogen oxide), it is able to combine with metal oxides or *basic oxides*, in general, forming *phosphates*, which correspond to sodium-dihydrogen phosphate. For instance, with cobalt oxide, sodium cobaltous phosphate, an intensely blue salt, is formed: $NaPO_3 + CoO \rightarrow NaCoPO_4$. The reactions, obtained with the metaphosphate bead, depend thus on the *acid character* of the bead, the metaphosphate being an *acid anhydride*, and on the capacity of the acid bead to form *salts* with *basic* or metal oxides. These salts are stable at the high temperature used, when the base is not volatile. When a *salt* of a volatile acid, *e.g.* $CoSO_4$, is fused with the metaphosphate bead, the salt is decomposed at the high temperature and loses its acid. $CoSO_4$ loses SO_3, ($CoSO_4 \rightarrow CoO + SO_3$), or H_2SO_4 (as a result of the decomposition of the salt by the water vapor in the flame); the metal oxide, CoO, combines with the metaphosphate to form a phosphate. Although phosphoric acid, in solution, is a much weaker acid than sulphuric acid, the fact that the metaphosphate is scarcely volatile enables it, in the flame test, to replace the sulphuric acid. The action of the metaphosphate bead on cobalt sulphate may then be summarized in the equation $NaPO_3 + CoSO_4 \rightarrow NaCoPO_4 + SO_3$. The salts of other volatile acids are decomposed in a similar way.

The salts formed with the various metal oxides frequently show characteristic colors, which are useful in identifying the oxides. When a metal forms more than one basic oxide, the corresponding phosphates may frequently

be obtained and the salt of the lower oxide may be converted, in the oxidizing zone of the flame, to a phosphate of the higher oxide and the latter may be reduced, in the reducing zone, to a salt of the lower oxide. Thus, iron forms, in the oxidizing flame, a pale yellow to brown (*hot* bead) ferric phosphate, which may be reduced to bottle green (*cold* bead) ferro- or ferro-ferric phosphate; the change of color is helpful in identifying iron in its salts.

As an *acid* anhydride, the metaphosphate bead tends to combine with, and to dissolve, *basic* oxides; but, as is to be expected, it shows little, if any, tendency to combine with *acid* oxides; thus, silicic acid is not appreciably dissolved by the metaphosphate bead, and if a silicate is heated in the bead, the metaphosphate, being present in large excess and being the stronger acid-forming oxide, decomposes the silicate and liberates the silicic acid in the form of an insoluble, semitranslucent mass — the so-called silicic acid " skeleton." For calcium silicate we would have $CaSiO_3 + NaPO_3 \leftrightarrows NaCaPO_4 + SiO_2$.

The Borax Bead. — Borax, $Na_2B_4O_7{,}10\,H_2O$, loses water, when it is heated in a flame, and melts to form a clear bead, similar to the metaphosphate bead. Like the latter, the borax bead is essentially the bead of a partial *acid anhydride* and may be said to contain sodium metaborate in combination with boric acid anhydride: $2\,NaBO_2 + B_2O_3 \rightarrow Na_2B_4O_7$ (whose structure is possibly $O:B-O-B(ONa)-O-B(ONa)-O-B:O$). As a partial acid anhydride, borax combines with basic oxides to form borates, just as sodium metaphosphate forms phosphates with the same oxides. The colors of the borax beads are also frequently used to identify metal oxides (*e.g.* the cobalt bead reaction, *q. v.*) In general, the chemistry of the borax bead reactions corresponds to that of the metaphosphate bead tests.

Ferric-ion, Fe^{+++}

1. Iron forms two common oxides, ferrous oxide, FeO, giving salts resembling, in general properties, those of the next group, in which they will be included, and ferric oxide, Fe_2O_3, whose salts resemble more those of aluminium and chromium. They are, therefore, included in the aluminium group.

(*a*) What class of reagents must be used to convert ferrous salts into ferric? and, conversely, ferric salts into ferrous?

(*b*) Dissolve part of a steel nail in hydrochloric acid, decant the solution, add some bromine-water to it and heat the mixture until no bromine odor remains. Note the change of color. What is formed?

(*c*) Pass hydrogen sulphide, in excess, through a dilute solution of ferric chloride and filter the solution. Note the change of color of the solution. Heat a little of the precipitate on a glass rod. What is it? What is the reaction?

2. (*a*) Test a solution of ferric chloride with neutral litmus paper. What does the result show as to the strength of ferric hydroxide as a base?

(*b*) Add sodium carbonate gradually to the solution and note everything that occurs. The precipitate is chiefly ferric hydroxide. Explain its formation. What connection has the conclusion, arrived at in (*a*), with the result of this test?

(*c*) Shake the solution of ferric chloride with an excess of barium carbonate suspended in water. Compare the result with (*b*) and compare it also with 6 (*b*) under "Aluminium-ion" and 3 under "Chromium-ion." *Aluminium, chromium and ferric chlorides and nitrates show this same behavior towards barium carbonate,* differing herein from the corresponding salts of the metals of the next (zinc) group. *Barium carbonate is used, therefore, as a group reagent to separate the two groups from each other.*

3. Add to ferric chloride solution some sodium hydroxide. Then add an excess of the alkali. Does the precipitate dissolve? Has ferric hydroxide sufficient acid properties to form a sodium salt in the presence of water? Compare it with aluminium hydroxide in this regard (p. 22, 1 (*b*)) and with chromium hydroxide (p. 25, 2). Arrange the hydroxides in the order of decreasing acid properties and note the corresponding order of the atomic weights of the elements.

4. Add to portions of a dilute solution of ferric chloride:

(*a*) Potassium ferrocyanide, $K_4[Fe(CN)_6]$. The precipitate is Prussian blue, $Fe_4[Fe(CN)_6]_3$, and is one of the most sensitive tests for ferric-ion.

(*b*) Potassium ferricyanide, $K_3[Fe(CN)_6]$.

(*c*) Ammonium thiocyanate NH_4SCN. This is the most sensitive test for ferric-ion. Take a single drop of ferric chloride solution, add it to 200 c.c. of water and test a portion in a test-tube for iron with thiocyanate; if no color shows, add a few cubic centimeters of ether and shake the mixture and note the color of the ether layer.

The color of ferric thiocyanate, $Fe(SCN)_3$, is not destroyed when its solution is warmed with alcohol (difference from a similarly colored solution produced by the action of nitrous acid on thiocyanates). In the presence of organic acids, the tests for ferric-ion must be made in a strongly acidified solution (see Chap. XII).

5. Add to a *freshly prepared* solution of potassium ferricyanide:

(*a*) Ammonium thiocyanate. Add ether and shake the mixture. Explain the absence of any red color. Recall the lecture experiment on the migration of ferricyanide ions.

Add a little concentrated hydrochloric acid to this mixture and shake it again with ether and note the appearance of a faint red tint against white paper. The explanation of this result will be given in the discussion of complex ions and their conditions of equilibrium (Chap. XII).

(*b*) Potassium ferrocyanide (fresh solution).

(*c*) Ammonium hydroxide.

6. Mix a good pinch of pulverized potassium ferrocyanide with an equal amount of dried, pulverized potassium *carbonate*, fuse the mixture in a test-tube held horizontally in the flame (hood!) until the whole mass has charred (*avoid inhaling any fumes of hydrocyanic acid, through the course of this experiment*), then, after the tube has cooled a few seconds, plunge (care!) the hot end of the test-tube into a small beaker of water (50 c.c.); allow the alkali salts to dissolve and the iron and carbon to subside, decant the liquid, and wash the residue twice with hot water. Treat the residue with dilute hydrochloric acid to dissolve the iron, filter the solution and oxidize the ferrous salt with a few drops of bromine-water and then add an excess of ammonium thiocyanate. If the experiment was carried out correctly, iron will be plainly indicated. Compare the result with 5 (*a*) and (*b*). The reactions are:

$$K_4Fe(CN)_6 + K_2CO_3 \rightarrow FeCO_3 + 6\ KCN.$$
$$FeCO_3 \rightarrow FeO + CO_2.$$
$$FeO + KCN \rightarrow KCNO + Fe.$$

7. Test a little of an iron salt with the borax or metaphosphate bead, in the oxidizing and the reducing zones of the Bunsen flame. Note the colors of the hot and the cold beads.

Characteristics of the Aluminium Group. — The hydroxides are very weak bases and very insoluble in water. They are precipitated by ammonium hydroxide even in the presence of ammonium chloride (difference from the alkali, the alkaline earth and the zinc groups) and by barium carbonate from a solution of the chlorides (difference from the zinc group). Only ferric sulphide is capable of existing in the presence of water and none of the sulphides is precipitated by hydrogen sulphide in the presence of hydrochloric acid (difference from the silver, copper and arsenic groups).

THE ZINC GROUP

Ferrous Iron, Nickel, Cobalt, Manganese and *Zinc*

Group Reactions. — 1. (*a*) Test a solution of nickelous chloride or nitrate with litmus. Is the hydroxide a very weak base? If in doubt, test a solution of ferric or aluminium chloride or nitrate with litmus and compare the result with that obtained with the nickelous salt.

(*b*) Add to the solution sodium carbonate. Does nickel form a carbonate stable in the presence of water? Cobaltous, ferrous, manganous and zinc salts show the same behavior. Compare this result with the behavior of aluminium, chromium and ferric salts. Which are the stronger bases, the bivalent hydroxides of this group or the trivalent ones of the previous group?

2. (*a*) Treat nickelous *chloride* or *nitrate* with suspended barium carbonate and filter the solution. Is the nickel precipitated? According to this result, which carbonate is less soluble in water, barium or nickel carbonate?

The same behavior toward barium carbonate is shown by ferrous, cobaltous, manganous and zinc chloride or nitrate.

(*b*) Mix a little ferric *chloride* and nickelous *chloride* or *nitrate*, and add to the mixture barium carbonate in excess. Filter the liquid and examine the color of the filtrate, concentrating the solution if necessary. This is the typical separation of the aluminium and zinc groups from each other.

(*c*) Treat nickelous *sulphate* with suspended barium carbonate and shake the mixture vigorously. Collect and wash the precipitate, dissolve it in dilute hydrochloric acid, and add ammonium sulphide to the solution. Is nickel carbonate precipitated from the sulphate solution by barium carbonate? Explain the difference in the result obtained in (*a*) and (*c*). May the sulphates be used in the separation of the aluminium and zinc groups?

3. Recall the results of experiments 9 (*a*) and (*b*) (p. 12) with manganous and ferric chlorides.

4. Use 0.1 molar solutions of ferrous, nickelous, cobaltous, manganous and zinc chlorides or nitrates for the following tests:

(*a*) Add to 10 c.c. of each solution some ammonium sulphide. Note the color of each precipitate. Are the precipitates sulphides or hydroxides? Make tests if in doubt. Compare the results with the behavior of aluminium and chromium, and correlate the facts with those obtained above in 1 (*b*) of this section.

(*b*) Pass hydrogen sulphide into 10 c.c. of each of the solutions.

(*c*) Add to 10 c.c. of each of the solutions 0.4 c.c. of hexanormal hydrochloric acid ("dilute hydrochloric acid") and pass hydrogen sulphide into each solution. *In the behavior toward hydrogen sulphide*, of the solutions *thus acidified*, lies the *typical analytical difference between the zinc group and the copper* (*silver*) *and arsenic groups.*

(*d*) Add to 10 c.c. of the solution of zinc, nickel or cobalt salt 10 c.c. of a molar solution of sodium acetate and 0.6 c.c. of hexanormal hydrochloric acid. Reserve a portion of the solution for (*f*) and saturate the remainder with hydrogen sulphide. To what difference in the composition of the solutions is the difference in this result and that obtained in (*c*) due?

(*e*) Put into each of five or six of the depressions of a white porcelain testing-tile[1] 0.1 c.c. of methyl violet solution.[2] To the solution, in one of the depressions, add 0.1 c.c. of 0.1 molar HCl, to a second the same amount of 0.25 molar acid, to a third the same quantity of 0.5 molar acid. The tint formed by the 0.25 molar acid may be used to recognize a concentration of hydrogen-ion, in which $[H^+]$ is approximately 0.2 to 0.27. This is the concentration of hydrogen-ion recommended for the separation of the copper and arsenic groups from the zinc group by hydrogen sulphide (see Chap. XII).

[1] Pipettes (graduated in 0.1 c.c.) should be used. Porcelain dishes or lids or tiles may be used. *Sufficiently accurate results may also be obtained readily as follows:* scratch five or six small marks with an "indelible ink" pencil (violet) on some sized paper or card and *make a test simply by applying a small drop of the acid liquid, at the end of a glass rod, to one of the dry marks:* 0.1 molar acid produces a blue tint, 0.25 molar acid the characteristic blue-green tint, 0.33 molar acid a yellow-green tint and 0.5 molar acid a yellow tint.

[2] A solution of 1:12,500 is used. The colored mass of violet "indelible ink" pencils usually consists of methyl violet, and such a pencil may be used, if the marks give the tints mentioned.

(*f*) Add to 10 c.c. of the nickel chloride solution 0.4 c.c. dilute hydrochloric acid (hexanormal) (as in (*c*)) and then add 0.1 c.c. of the mixture to 0.1 c.c. of the methyl violet solution (or *apply the test described in footnote* 1, p. 31). Finally, add 0.1 c.c. of the mixture of nickel chloride, sodium acetate and hydrochloric acid, obtained in (*d*), to another portion of the methyl violet solution and note the result.

In addition to these general group reactions of the ions of the metals of the zinc group, which are used in separating the group from other groups, the characteristic reactions, for separating the members of the group from each other and for identifying them, must be studied.

Ferrous-ion, Fe^{++}

1. Prepare a fresh solution of ferrous ammonium sulphate[1] and test the solution with: (*a*) potassium ferrocyanide; (*b*) potassium ferricyanide; (*c*) potassium thiocyanate. Compare the results with those obtained with ferric salts in the analogous experiments (p. 28). How would we recognize ferrous and ferric salts in the presence of each other?

2. Recall the metaphosphate and borax bead tests with iron salts (see Ferric-ion, § 7, p. 29).

Nickel-ion, Ni^{++}; *Cobalt-ion*, Co^{++}

1. Test a *little* of a salt of each metal with the borax bead. Mix approximately equal parts of the salts, and test the mixture with the borax bead.

2. Use a few cubic centimeters of the solution of some nickel salt for each of the following tests, the reagent to be added being given. Then make the same tests with a cobalt salt and note all the results:

(*a*) An excess of sodium hydroxide. Have the hydroxides acid properties?

(*b*) An excess of ammonia.

(The chemistry of this reaction is considered in connection with the next group in Chap. XII.)

---

[1] A bluish tint obtained in (*a*) or a pink tint in (*c*) would indicate contamination with traces of ferric salt.

(*c*) An excess of ammonium sulphide. Filter the liquid and note the characteristic difference between nickel and cobalt. Boil the filtrate from the nickel sulphide, after acidifying it slightly with acetic acid. This is an important reaction of *nickel* by means of which its presence may often be most easily discovered.

3. Add to 10 c.c. of a nickel or cobalt salt solution:

(*a*) A few drops of hydrochloric acid and then pass hydrogen sulphide in excess into the solution.

(*b*) A few drops of ammonium sulphide. Decant the liquid from the precipitate and then add quite dilute hydrochloric acid (molar) to the precipitate.

What is there that is remarkable in the fact that (*a*) and (*b*) *seem* to lead to a *different* result (see Chap. X)?

4. Test a solution of a nickel salt as follows, noting all the results, and then test a cobalt salt in the same way (see Addenda, p. 149):

(*a*) Add an excess of sodium hydroxide and then bromine-water. The black precipitates are nickelic hydroxide, $Ni(OH)_3$, and cobaltic hydroxide, $Co(OH)_3$.

(*b*) Add (in a porcelain dish) a solution of potassium cyanide, *drop by drop*, until the precipitate first formed by the cyanide has just redissolved, then add a few *drops* excess of the reagent. (*Note:* Great care must *always* be used in handling potassium cyanide, which is a *deadly poison.* Precautions are given on the reagent bottle and *should be observed.*) Warm the solution, add to it 5 to 10 c.c. of sodium hydroxide solution and an excess of bromine-water. Heat the mixture. This reaction gives us a good method for determining *nickel* in the presence of cobalt (see Chap. XII). For a second method, without cyanide, see p. 149.

Test, by either method, 20 c.c. of cobalt sulphate or chloride solution for the *trace* of *nickel* salt that is found in cobalt salts, which are not most carefully purified.

(*c*) Add some acetic acid and a large *excess* of potassium nitrite and warm the solution. Cobalt salts give a precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$, aq. This reaction gives us a good method for determining *cobalt* in the presence of nickel.

Test, by this method, 10 to 20 c.c. of nickel sulphate or chloride solution for the *trace* of *cobalt* salt that usually contaminates nickel salts; let the mixture stand twenty-four hours.

Zinc-ion, Zn^{++}*, and Zincate-ion,* $ZnO_2^{=}$

1. Test a zinc salt with the borax bead. Heat some zinc salt, moistened with a tiny drop of cobalt nitrate solution, on a piece of charcoal, with the blowpipe.

2. Add to a zinc salt solution gradually:

(*a*) An excess of sodium hydroxide. Has zinc hydroxide any acid properties? (Difference between zinc hydroxide and the other hydroxides of this group.)

(*b*) An excess of ammonia (see Chap. XII).

(*c*) (1) Hydrogen sulphide in *excess:* filter the solution and add ammonium hydroxide and ammonium sulphide to the filtrate.

(2) A few drops of hydrochloric acid and then hydrogen sulphide.

Consider the ionization equilibrium for hydrogen sulphide and explain briefly the difference in the results of (*c*) (1) and (2).

3. The most sensitive test for zinc salts is afforded by its spectrum. A drop of a solution may be tested with the aid of an electric spark; 0.001 milligram can be identified with certainty in a drop, the characteristic zinc lines flashing up occasionally (p. 14). A group of three blue lines, whose wave lengths are 481, 472 and 468 $\mu\mu$, and a red line (636 $\mu\mu$) are most characteristic.

Manganese; Manganous-ion, Mn^{++}

1. What oxides does manganese form (read Smith or Remsen)? Which have base-forming properties, which acid-forming? How does the character change with the increasing amount of oxygen in the oxides? From which oxide are the common salts, the chloride, sulphate, etc., derived? From which oxide are the permanganates derived?

(*a*) Fuse a minute quantity of any manganese compound with a little sodium carbonate and potassium chlorate, in the loop of a platinum wire, at the outside edge of the flame. This affords a sensitive and characteristic test for manganese. Sodium manganate Na_2MnO_4 is formed.

(*b*) Heat a very small amount of a manganous salt with lead dioxide and nitric acid to boiling and allow the liquid to clarify (the lead compound must be free from manganese; test it by

making a blank test). This reaction gives another sensitive test for manganese. The product is permanganic acid, $HMnO_4$. The dilute solution gives very characteristic absorption bands when examined with a spectroscope (p. 24). Chlorides should be absent.

2. Add to a manganous salt solution: (*a*) sodium hydroxide in excess; (*b*) ammonia solution in excess; (*c*) acetic acid and hydrogen sulphide. Compare the results with those obtained with Zinc-ion, § 2, p. 34.

Characteristics of the Zinc Group. The hydroxides of the group are moderately strong bases. They form difficultly soluble sulphides and carbonates, which are *stable* in the presence of water; the hydroxides, although little soluble, are sufficiently soluble not to be precipitated by ammonium hydroxide in the presence of ammonium chloride (differences from the aluminium group). The sulphides are precipitated by ammonium sulphide in neutral or alkaline solutions (difference from the aluminium, alkaline earth and alkali groups), but are not precipitated by hydrogen sulphide in moderately acid solutions (difference from the copper and arsenic groups).

Ask for an "unknown" mixture of salts of ions of the aluminium and zinc groups.

ANALYSIS OF THE ALUMINIUM AND ZINC GROUPS

I. *Precipitation of the Aluminium and Zinc Groups (Separation from the Alkalies and the Alkaline Earths)*

1. First add 10 c.c. ammonium chloride reagent to the solution, then ammonium hydroxide until the solution is slightly alkaline, disregarding the formation of any precipitate, and finally add a small *excess* of ammonium sulphide. In this way Al^{+++}, Cr^{+++}, Fe^{+++}, Fe^{++}, Mn^{++}, Zn^{++}, Ni^{++}, Co^{++} are separated[1] from Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++} and the alkali metal ions. (Why is ammonium chloride used?) When you have found, by test, that sufficient ammonium sulphide has been added, boil the mixture for a few minutes, then transfer the precipitate (P) to a filter, reserve the filtrate for examination according to 2, and wash the precipitate

---

[1] A complication ensues if phosphate, borate or some similar ions, which form insoluble alkaline earth salts, are present; it is discussed and provided for in Part IV on Systematic Analysis.

with 25 c.c. of water, to which a little ammonium sulphide and 3 to 5 grams of ammonium chloride or nitrate[1] have been added.

2. *Filtrate.* If the filtrate is brown, a trace of **nickel** is indicated. To find it, remove the ammonia by boiling the solution under a hood, or make the solution faintly acid with acetic acid; the slight precipitate is collected upon a small filter paper, the paper incinerated and the ash tested with a minute borax bead.

3. *Precipitate* (P). What substances may be present in this precipitate? Write the formulæ of all of the possible compounds. Put the precipitate in a beaker and treat it with an excess (at most 100 to 150 c.c.) of cold, very dilute hydrochloric acid (one volume of dilute acid (hexamolar) with four volumes of water). Add the acid gradually as long as there is evolution of hydrogen sulphide, then filter the solution at once. A black residue (R) may contain **nickel** and **cobalt** sulphides, the acid solution (S) may contain salts of the remaining ions of the groups, besides small quantities of nickel and cobalt.

II. *Analysis of the Residue* (R) *insoluble in Dilute Hydrochloric Acid. Determination of Cobalt and Nickel*

1. Test the residue with the borax bead. Either **cobalt** or **nickel** will be recognized or a mixture of both indicated.[2]

2. If the test showed **cobalt,** test for **nickel** as follows:[3] Dissolve about half of the residue (R) in a *little* concentrated hydrochloric acid and a little nitric acid, evaporate the solution on a water bath almost to dryness, dissolve the residue in water and a few drops of hydrochloric acid, then add sodium hydroxide to alkalinity and a very little acetic acid until the solution is again *slightly* acid to litmus paper. (X.)[4] Add to the solution, in an

---

[1] The ammonium sulphide prevents oxidation of the sulphides, the ammonium chloride or nitrate prevents their forming *colloidal* suspensions (Chap. VII).

[2] According to Curtman and Rothberg (*J. Am. Chem. Soc.*, **33**, 188 (1911), a mixture of cobalt and nickel sulphides, containing as little as 3% of cobalt sulphide, gives a blue bead; with 2.5%, an uncertain brownish bead is produced, and with 2% or less, a brown bead.

[3] Read the whole method first. (*To avoid cyanide* see Addenda, p. 149.)

[4] This is merely a sign for future reference.

evaporating dish, a dilute solution of potassium cyanide (Poison! Care!), *drop by drop*, until any *colored* precipitate, which may form, is just redissolved (not the colorless silica or alumina which sometimes appears); then add only two or three drops more of the potassium cyanide solution. If no heavy precipitate is formed by the first two or three *drops* of the cyanide, not more than three or four more *drops* are added. Warm the solution gently. Add 40 to 50 c.c. of sodium hydroxide solution and then an excess of bromine-water. Let the bromine-water float first on top of the liquid, to get a *local excess*, and observe whether a *black coloration* appears. If it does show, it may disappear when the liquid is stirred, but then a black precipitate will finally result, if *sufficient* bromine-water and sodium hydroxide are used. Heat the solution, collect any black precipitate on a small filter, *wash it thoroughly* with hot water, and test the precipitate with the borax bead to confirm **nickel.**

N.B. A large excess of potassium cyanide must be avoided because nickelic hydroxide cannot be precipitated until the excess is destroyed by the bromine. A few drops excess is all that is required to prevent the precipitation of cobalt. (In case of a negative result, consult the instructor before throwing away solutions, etc.)

3. Test for **cobalt** by the potassium nitrite method. Proceed with (**R**) as above in § 2 to the point marked (X) (*do not add potassium cyanide*), then add more acetic acid and precipitate $K_3Co(NO_2)_6$ with a large excess of potassium nitrite, allowing the mixture to stand some time in a warm place. Confirm **cobalt,** in the precipitate, with the borax bead if a blue bead was not obtained in § 1.

III. *Analysis of Solution* (**S**): *Determination of Iron; Separation of Iron, Chromium and Aluminium from Manganese and Zinc* (*traces of Nickel and Cobalt*)

1. *Boil the solution* (**S**) *to remove hydrogen sulphide*, add a *little* potassium chlorate or bromine-water to the hot solution, until the odor of chlorine or bromine is perceived, and remove the excess of bromine or chlorine by boiling the solution; cool the solution and test a *small portion* for **ferric-ion** by means of ammonium thio-

cyanate or potassium ferrocyanide. Test the original unknown for **ferrous-ion** (p. 32, 1 (*b*) and **ferric-ion** (p. 28, 4 (*a*) or 4 (*c*)).

2. Neutralize the rest of the (*cooled*) solution, obtained in § 1, by adding sodium carbonate until a *permanent* precipitate is formed. Redissolve this precipitate in hydrochloric acid, which must be added only until the precipitate has *just disappeared.* To this *slightly* acid solution, add an excess of a suspension of *solid barium carbonate* in water. Shake or stir the solution with the barium carbonate until the supernatant liquid is at most slightly colored, if colored ions (Fe^{+++}, Cr^{+++}) are present, otherwise five minutes shaking will do.[1] Collect the precipitate (**PP**) and test it for **chromium** and **aluminium** (IV, 1 or 2), and examine the filtrate (**FF**) for **manganese** and **zinc** and traces of nickel and cobalt (V).

IV. *Examination of the Precipitate* (**PP**) *for Chromium and Aluminium*

Use method § 1 or 2.

1. Add to a part (one-fourth) of the precipitate (**PP**) 3 to 5 c.c. of water and a small amount of sodium peroxide (care!), then heat the mixture to boiling. A *yellow* solution of sodium chromate proves the presence of **chromium.** The solution is filtered and to a small portion (1 c.c.) of it sufficient acetic acid to render the solution acid and a few drops of lead acetate solution are added. A bright yellow precipitate of lead chromate is formed if **chromium** is present. The rest of the solution is acidified with nitric acid, boiled, rendered slightly alkaline by ammonium hydroxide solution, and boiled once more. A flocculent white precipitate is **aluminium** hydroxide. A confirmative test of the washed precipitate is made with cobalt nitrate (§ 7, p. 24).

2. A part of the precipitate (**PP**) is examined for **chromium** by being fused with some sodium carbonate and potassium chlorate. The fused mass is extracted with a little water and the extract is filtered. If the mass was green (**manganate**), boil the solution with a single drop of alcohol and filter it again, if necessary. In either case, if the filtrate is yellow (compare the tint, if faint, with that of pure water) chromic acid is present. The addition of lead acetate and acetic acid will give yellow lead **chromate.**

---

[1] Chromium salts are decomposed more slowly than aluminium and ferric salts.

Test a larger portion (one-fourth) of the precipitate (PP) for *aluminium* by boiling it with 5 c.c. water to which a gram of solid barium hydroxide and an equal amount of sodium carbonate have been added; filter, acidify (with HCl) and boil the solution, and add ammonium hydroxide in *slight* excess (litmus). A flocculent precipitate shows the presence of **aluminium.**[1] A confirmative test of the washed precipitate is made with cobalt nitrate (§ 7, p. 24).

V. *Analysis of the Filtrate* (FF) *for Manganese and Zinc* (*and Traces of Nickel and Cobalt*)

1. (*a*) Heat the filtrate (FF) to boiling and add a small excess of sulphuric acid slowly to the boiling liquid, to precipitate barium sulphate. Filter the solution, and concentrate it to 10 to 15 c.c.

(*b*) Precipitate **manganese** and **zinc,** together with possible small quantities of **nickel** and **cobalt,** as sulphides, by means of ammonium hydroxide and ammonium sulphide added to the boiling solution. The mixture is heated for two or three minutes. The precipitated sulphides are transferred to a filter and treated according to § 2, if nickel and cobalt have already been found in section II above, and according to § 3, if nickel or cobalt has not yet been found in the unknown.[1]

---

[1] A very slight precipitate may be silicic acid, if the latter, when present, has not been excluded by the previous treatment of the solution of an unknown (silicate analysis, *q. v.*); barium silicate, while it is insoluble in water, is somewhat decomposed by a boiling solution of sodium carbonate. A further test may be made in either one of the following ways. Ammonium hydroxide solution *free from carbonate* is required for (*a*), and if none, of the required degree of purity, is at hand, the longer method given in (*b*) must be used. The ammonium hydroxide solution is tested by adding five or six drops of it to a clear barium chloride solution; no turbidity, $BaCO_3$, should be formed.

(*a*) A portion of the precipitate (PP) is boiled with barium hydroxide and water, *without the addition of sodium carbonate*, and the solution treated otherwise as explained in the text.

(*b*) The flocculent precipitate, obtained by the process described in the text, is allowed to settle (a centrifugal machine is used, with advantage, for the purpose), the supernatant liquid is decanted, and the precipitate dissolved in two or three drops of hydrochloric acid. The solution is evaporated to dryness in a small dish, the residue dried 15 minutes at 120° and then warmed with a drop or two of hydrochloric acid and extracted with 1 to 2 c.c. of water. The solution is filtered, boiled and rendered slightly alkaline with ammonium hydroxide. A precipitate is **aluminium hydroxide.**

2. The sulphides are treated with an excess of diluted hydrochloric acid (one part hexamolar acid to four parts of water).

A small dark residue, remaining undissolved, would be nickel or cobalt sulphide; these sulphides are not altogether insoluble in the acid as used in section I (see Chap. X).

(*a*) Filter the solution from any such dark residue, boil the filtrate and expel the hydrogen sulphide *completely*. Cool the solution and add sodium hydroxide in excess to it. If a precipitate forms, collect it upon a filter paper, and test it for **manganese** by means of lead dioxide (see § 1 (*b*), p. 34) or by fusing some of it with sodium carbonate and potassium chlorate (p. 34, § 1 (*a*)). If the precipitate is small, incinerate the paper and test the ash.

(*b*) The alkaline solution, which has been separated from the manganese, is tested for **zinc** by the addition of hydrogen sulphide *water*. The characteristic spark spectrum furnishes the best confirmative test for **zinc** (§ 3, p. 34).

3. If nickel or cobalt has not been found previously, the sulphide precipitate, obtained in § 1 of this section, is treated with 25 c.c. of a 5 per cent solution of acetic acid, which has previously been saturated with hydrogen sulphide. Manganese sulphide, if present, is dissolved by this acid (solution S′), the sulphides of zinc, nickel and cobalt (residue **R′**) are not dissolved.

(*a*) The solution (S′) is examined for **manganese** according to § 2 (*a*).

(*b*) The residue (**R′**) is dissolved in a little hot dilute hydrochloric acid, the solution is boiled to remove all traces of hydrogen sulphide and then cooled; an excess of sodium hydroxide is then added to it. A precipitate (**nickel** or **cobalt** hydroxide) is collected on a filter and examined for **nickel** and **cobalt** according to section II, and the filtrate from the precipitate is tested for **zinc** by the addition of hydrogen sulphide water. The spark spectrum furnishes the best confirmative test for **zinc** (§ 3, p. 34).

---

[1] C. S. Tingley (*Master's Dissertation*, The University of Chicago, 1909) found that 1 mg. of zinc, nickel, cobalt or manganese can be readily detected in mixtures by the scheme of analysis given in sections I to V.

THE SILVER AND COPPER GROUPS

Silver Group: Silver, Lead and (Mercurous) Mercury. Copper Group: (Mercuric) Mercury, (Lead), Bismuth, Copper and Cadmium (Complex Ions and their Instability Constants)

Group Reactions. — Use 0.1 molar solutions of silver, lead, mercurous, mercuric, bismuth, copper and cadmium nitrates for the following tests:

1. Add 1 c.c. of hydrochloric acid to 10 c.c. of each solution (*difference between the silver and copper groups*).

2. (*a*) Add to 10 c.c. of each of the solutions 0.4 c.c. of hexamolar nitric acid and pass hydrogen sulphide into the acidified solutions. Note the colors of the precipitated sulphides. Compare the behavior of these solutions with the behavior of the ions of the zinc group under the same conditions (p. 31, § 4 (*c*)).

What is the action of a strong acid on the condition of equilibrium of hydrogen sulphide and its ions? To what is the difference in behavior of the salts of the two groups due?

(*b*) Add to 10 c.c. of the 0.1 molar cadmium nitrate solution 2 to 3 c.c. concentrated hydrochloric acid and pass hydrogen sulphide into the solution as long as it is absorbed. Then dilute the mixture with four or five volumes of water and pass more hydrogen sulphide into the solution. Explain the results on the basis of the conditions of chemical and physical equilibrium obtaining. Lead salts behave much in the same way in the presence of a large excess of hydrogen-ion.

(*c*) Repeat (*b*) with copper nitrate. Explain the difference in the results of (*b*) and (*c*) (Chap. XI).

Under what conditions must we use hydrogen sulphide to get a complete precipitation of this group?

3. Precipitate bismuth sulphide as in 2 (*a*), filter and wash the precipitate and digest it then with several cubic centimeters of ammonium sulphide. Does it dissolve perceptibly? Filter the liquid from the precipitate and add dilute hydrochloric acid to the filtrate. Is any bismuth sulphide reprecipitated?

The behavior of bismuth sulphide is typical for all the sulphides of the group and distinguishes them from the sulphides of the metals of the arsenic group.

N. B. *Copper* sulphide is very sparingly soluble in ammonium sulphide, *mercuric* sulphide is sparingly soluble in sodium or potassium sulphide (see Chap. XIII).

Silver-ion, Ag^+

1. (*a*) Test the silver nitrate solution with neutral litmus. Is the nitrate the salt of a weak or a strong base?

(*b*) Add sodium hydroxide in excess to silver nitrate. Has the silver oxide (silver hydroxide) any tendency to form a sodium salt or any acid properties?

(*c*) Add ammonia solution, drop by drop, in excess, to silver nitrate solution. The precipitate dissolves readily in excess of ammonia. Can this be due to any acid properties of silver hydroxide and to the formation of an "ammonium argentate"? Which would form a salt more readily with a weak acid, sodium hydroxide or ammonium hydroxide? Justify your conclusion either by the laws of equilibrium or by recalling experimental facts bearing on the question.

2. Ammonia forms a complex positive ion with silver (Chap. XII), according to the following equation:

$$Ag^+ + 2\,NH_3 \rightleftarrows Ag(NH_3)_2^+$$

Apply the law of chemical equilibrium to this system and express, mathematically, what ratio would be constant in the system. If we put the concentration of the complex ion in the denominator, the constant has the value $k = \frac{1}{10^7}$, and is called the *instability constant* of the complex ion. According to this value, can there be many silver ions in an ammoniacal silver solution? Might it be possible to precipitate *any* silver salts, at all, from such a solution? (Test your conclusion, presently, according to (*a*) below.) Will silver salts be precipitated as easily from an ammoniacal solution as from a silver nitrate solution (see (*b*))? What effect will a considerable *excess* of *ammonia* have on the concentration of the silver ions according to the above equation? Will it facilitate the precipitation of silver salts (see (*c*))?

Add to 20 c.c. of 0.25 molar $AgNO_3$ solution (desk reagent) hexamolar ammonia solution, from a graduated 2 c.c. pipette, until the precipitate of silver oxide has just redissolved (1.7 c.c. will

be required) and then add an excess of 0.3 c.c. (2 c.c., in all, being added). Use the solution for the experiments (*a*), (*b*) and (*c*).

Calculate from the concentrations and the volumes of silver nitrate and ammonia (1.7 c.c.), used to give a clear solution, in what ratio, in molecules, ammonia combines with silver nitrate.

(*a*) Add to 5 c.c. of the solution 5 c.c. 0.1 molar sodium chloride solution.

(*b*) Add a few drops of sodium chloride and sodium phosphate solutions to separate portions of silver nitrate. Then add 5 c.c. 0.1 molar sodium phosphate solution to 5 c.c. of the ammoniacal silver solution prepared above. Why is silver chloride precipitated in the ammoniacal solution and silver phosphate not? Devise a simple experiment to test your conclusion (Chap. IX).

(*c*) To another 5 c.c. of the ammoniacal silver solution, add a larger excess (2 or 3 c.c.) of ammonia, and then add sodium chloride, as in (*a*). Explain the difference between (*a*) and (*c*). Is the silver-ion completely suppressed? Add a drop of ammonium sulphide to part of the ammoniacal silver solution containing the larger excess of ammonia and then answer the question.

(*d*) To the solution (*c*), in which sodium chloride failed to give a precipitate, add, after the sodium chloride, nitric acid in *excess*. Explain the effect of the nitric acid, on the basis of the equilibrium equation established above.

Silver-ion is identified by the precipitation of its difficultly soluble chloride, by the solubility of the latter in excess of ammonia and by the reprecipitation of the chloride when the ammoniacal solution is neutralized.

3. Add potassium cyanide solution (care!) slowly to 20 c.c. of silver nitrate, until the precipitate first formed has just redissolved. Silver-ion forms with cyanide-ion *complex negative ions* (Chap. XII), as do cobalt, nickel, ferrous, ferric, cupric and cuprous ions and many other ions. For the silver-ion we have

$$K^+ + Ag^+ + 2\,CN^- \rightleftarrows K^+ + [Ag(CN)_2^-] \rightleftarrows K[Ag(CN)_2]$$

or

$$Ag^+ + 2\,CN^- \rightleftarrows [Ag(CN)_2^-]$$

Give the mathematical equilibrium equation for the last equation. Judge from the result of experiments in §2 above and from the following, *which is the more stable*, the complex ion of silver-ion with ammonia or the complex ion of silver-ion with the cyanide-ion:

(*a*) To a portion of the solution of $K[Ag(CN)_2]$ add some sodium chloride.

(*b*) To a second portion, add some ammonium sulphide. Then add to the mixture potassium cyanide until the precipitated sulphide has redissolved.

(*c*) Recall 5 (*a*) under Fe^{+++} (p. 29) and 4 (*b*) under Ni^{++} and Co^{++} (p. 33). What could you say of the value of the instability constant of the ferricyanide ion $Fe(CN)_6^{\equiv}$? of the cobalticyanide ion $Co(CN)_6^{\equiv}$? Explain now the effect of concentrated hydrochloric acid on ferricyanides (5 (*a*), p. 29), using the equilibrium equation for the complex ion and the fact that hydrocyanic acid is an extremely weak acid (Chap. XII).

4. Precipitate some silver chloride, bring it on a filter and expose some of it to sunlight. Mix another small portion with sodium carbonate and heat the mixture on charcoal with a blowpipe. Cut out the contents of the cavity, treat the mass with water in a mortar, throw away the floating particles and rub the heavier particles in the mortar vigorously with a pestle.

Lead-ion, Pb^{++}, *and Plumbite-ion*, $PbO_2^{=}$

1. Repeat with lead nitrate § 1 (*a*), (*b*), (*c*) described under *Silver-ion*. Has lead hydroxide any acid properties? Does lead-ion resemble silver-ion in its behavior toward ammonia?

2. To 10 c.c. of a solution of lead nitrate add hydrochloric acid. Bring the precipitated chloride on a filter and wash it with some water.

(*a*) Treat about half of the lead chloride with 50 c.c. boiling water. It is quite soluble in hot water, *differing in this respect from silver and mercurous chlorides*. Cool the solution, decant or filter it from the separated crystals and use the solution for (*b*) and (*c*).

(*b*) Add hydrogen sulphide to a part of the filtrate. Is lead chloride insoluble in *cold* water? Add to another portion sulphuric acid. Is the sulphate less soluble than the chloride?

(*c*) Add to a further portion of the cold solution of lead chloride potassium chromate. Let the precipitate subside, decant

the liquid and add sodium hydroxide to the precipitate. Why does the precipitate dissolve? (See § 1 (*b*).) Add acetic acid to the alkaline solution. The lead chromate will be reprecipitated. *Lead-ion is best identified by this series of reactions.* Give their equations.

3. Mix a portion of the solid lead chloride obtained in § 2 with some sodium carbonate and reduce it to lead in the reducing flame of the blowpipe.

Mercury; Mercurous-ion, Hg^+

1. Add to separate portions of a solution of mercurous nitrate: (*a*) sodium hydroxide in excess; (*b*) ammonia in excess; (*c*) hydrochloric acid. What is the familiar name of the last precipitate? Decant the liquid, wash the precipitate once with water by decantation and then treat a portion of the precipitate with hot water, another portion with ammonia. (*Difference from lead and silver chlorides.*) The *black* product of the action of ammonia on mercurous chloride is a mixture of finely divided mercury and of mercuri-ammonium chloride, NH_2HgCl. *Mercurous-ion* is identified by this action.

2. Mix a little dry mercurous or mercuric salt with dry sodium carbonate in a narrow glass tube, three inches long and closed at one end. Cover the mixture with a little pure dry sodium carbonate, leaving two inches of the tube free, and heat the contents, advancing from the pure carbonate to the mixture. Give the equations for the action.

Mercury; Mercuric-ion, Hg^{++}

1. Add to separate portions of a solution of mercuric nitrate: (*a*) sodium hydroxide in excess; (*b*) ammonia in excess; (*c*) hydrochloric acid.

2. Treat mercuric chloride solution with stannous chloride in excess. Mercurous chloride and then mercury are precipitated. *Mercuric-ion* is identified by this action. Give the equations of the reactions. What is the familiar name for mercuric chloride?

3. See, above, the behavior of mercuric salts when heated with sodium carbonate (§ 2 under *Mercurous-ion*).

Copper; Cupric-ion, Cu^{++}

1. Add to separate portions of a solution of cupric sulphate:[1] (*a*) sodium hydroxide in excess; (*b*) ammonia in excess (Is a complex ion formed with the ammonia?); (*c*) hydrochloric acid; (*d*) potassium cyanide[1] (care!), added drop by drop, until the precipitate has redissolved, and then a few drops excess. Copper forms with cyanide-ion complex ions of great stability, similar to the complex ions of silver-ion and cyanide-ion (p. 43). Cupric-ion is readily reduced by the cyanide and the solutions obtained with excess of cyanide contain chiefly potassium *cupro*-cyanide, $K_2Cu(CN)_3$ (Chap. XII). Judge of the stability of the complex cyanide-ion, as compared with that of the complex cupriammonium-ion, by the following tests:

(1) Add a considerable excess of ammonia to some copper sulphate. To a portion add ammonium sulphide.
(2) To a portion of the cyanide solution obtained in (*d*) add ammonium sulphide.
(3) To some of the blue solution (1) add a few crystals of potassium cyanide until the blue color is discharged.

2. (*a*) Add to cupric sulphate some potassium ferrocyanide. This is a most sensitive test for *cupric-ion.*

(*b*) Heat a copper salt with sodium carbonate in the reducing flame before the blowpipe. Treat the mass according to § 4 under *Silver-ion,* p. 44.

(*c*) Heat a little copper salt with a borax bead in the oxidizing flame; then heat it in the reducing flame, after adding a very little stannous chloride.

(*d*) Heat some cupric chloride on the end of a copper (or platinum) wire.

Cadmium-ion, Cd^{++}

1. Add to separate portions of a solution of cadmium nitrate:[1] (*a*) an excess of sodium hydroxide; (*b*) an excess of ammonia; (*c*) hydrogen sulphide (recall 1 (*b*), p. 41, of the group reactions of the silver and copper groups); (*d*) a small excess of potassium cyanide; then add some ammonium sulphide to the solution (*difference from copper*).

---

[1] See Addenda, p. 149.

2. Heat some cadmium salt with sodium carbonate in the reducing flame of the blowpipe. Note the brown coating of cadmium oxide surrounding the cavity in the charcoal. What does the presence of this coating show as to the volatility of metallic cadmium?

3. *Cadmium-ion* is usually identified by means of its *yellow sulphide*, which is insoluble in ammonium sulphide (*difference from* the yellow sulphides of *arsenic* and (stannic) *tin*). We can, further, identify it, with greatest certainty, by means of the spectroscope, the electric spark being used with a drop of a solution (see p. 12). As little as 0.0001 milligram can be identified in a drop of liquid. A group of three (green and blue) lines, whose wave lengths are 509, 480 and 468 $\mu\mu$, and a (red) line (644 $\mu\mu$) are the most characteristic. The general character of the spectrum shows a striking resemblance to that of zinc, which is in the same family of the periodic system.

Bismuth-ion, Bi^{+++}

1. Test a solution of bismuth nitrate with litmus. What would you say as to the strength of bismuth hydroxide as a base?

2. Add to bismuth nitrate solution: (*a*) sodium hydroxide in excess; (*b*) ammonia in excess. Use the precipitate for § 3.

3. Transfer the precipitated bismuth hydroxide to a filter, dissolve it in hydrochloric acid, and add water to the solution. The precipitate is bismuth oxychloride, a basic bismuth chloride, formed according to

$$BiCl_3 + H_2O \rightleftarrows (BiO)Cl \downarrow + 2\,HCl.$$

Under what conditions will the test be most sensitive, in the presence of much or little hydrochloric acid, much or little water? Properly applied, *this is one of the best tests for bismuth-ion.*

4. Add to a little stannous chloride an excess of sodium hydroxide and to the solution of sodium stannite, thus formed, add a few drops of a solution of a bismuth salt. A brown precipitate is bismuthous oxide, a black one is bismuth. This is another *very sensitive test for bismuth-ion.*

5. Bismuth gives also a characteristic spark spectrum. The most characteristic line has a wave length of 472 $\mu\mu$; less brilliant lines have wave lengths of 555, 521 and 412 $\mu\mu$.

6. Reduce some bismuth salt before the blowpipe. The globules of the metal are quite brittle.

Characteristic Properties of the Silver and Copper Groups.— The *hydroxides* of the metals of these groups are pronounced bases; only lead hydroxide is amphoteric, but its basic character predominates.

The *sulphides* of the metals of these groups are more insoluble in water than those of the previous groups, and are precipitated by hydrogen sulphide even from solutions containing a moderate excess of a strong acid (difference from all the previous groups).

The *sulphides* have no acid-forming properties and are insoluble in ammonium sulphide[1] (difference from the arsenic group). All the sulphides, excepting the sulphide of mercury, dissolve in hot dilute nitric acid.

Silver, mercurous and *lead* ions form *difficultly soluble chlorides* and advantage is taken of that fact to separate them, as a group, from the other analytical groups of metal ions. Lead chloride, however, is sparingly soluble in water, and, if present in small quantity, lead is found in the copper group rather than in the silver group.

ANALYSIS OF THE SILVER AND COPPER GROUPS

I. *Precipitation of the Silver Group*

Add to the aqueous or nitric acid solution dilute hydrochloric acid, drop by drop, as long as a precipitate forms, and then an excess of ten or twelve drops, to redissolve any bismuth oxychloride. Bring the precipitated chlorides (**P**) on a filter and wash them twice with 10 c.c. of cold water. Reserve the filtrate (**F**), together with the washings, for further analysis according to III.

II. *Analysis of the Precipitate* (**P**) (SILVER GROUP)

1. Pour 3 or 4 c.c. hot water over the precipitate (**P**) on the filter, and test the liquid running through the filter for **lead** according to p. 44, 2 (*c*) under *Lead-ion.* If **lead** is found, extract the precipitate (**P**), in a dish or beaker, with boiling water, until

---

[1] See the note, p. 42, in regard to the slight solubility of cupric sulphide in ammonium sulphide and of mercuric sulphide in sodium or potassium sulphide.

sulphuric acid (§ 2 (*b*), p. 44) shows the washings are free from lead-ion.

2. Treat the residue with ammonia; a black product is evidence of the presence of **mercurous** chloride. It is washed with ammonia and water, and treated with hydrochloric acid and a few crystals of potassium chlorate; the solution is diluted and filtered and treated with stannous chloride; a white or gray precipitate confirms the presence of **mercurous** chloride in (P).

3. The ammoniacal filtrate, obtained in § 2, is acidified with nitric acid, used in small *excess* (test). A precipitate shows the presence of **silver.**

NOTE: *Lead* chloride is sparingly soluble in water and it cannot be completely precipitated; small quantities of lead would not be precipitated at all as chloride, but would be found only in the copper group.

III. *Analysis of the Filtrate* (F) (COPPER GROUP)

1. Into the filtrate (F) pass hydrogen sulphide in excess (test?). Then dilute the mixture, without filtration, to 100 c.c. and test the solution by means of methyl violet (the method is described on p. 31), in order to determine the strength of the acid. If a blue-green or blue tint is produced, the concentration of the hydrogen-ion is not too great for the precipitation of traces of cadmium-ion and lead-ion; saturate the mixture once more with hydrogen sulphide and collect the sulphides on a filter. They are washed[1] twice with hydrogen sulphide water and examined according to § 2. If the methyl violet test shows that an undue excess of acid is present (yellow or yellow-green tint), collect any sulphide precipitate, and wash it as directed above; evaporate the filtrate to dryness, redissolve the residue in 3 or 4 c.c. of dilute hydrochloric acid and 100 c.c. of water and treat the solution once more with hydrogen sulphide. If a precipitate is formed, it is collected on a filter, washed, and combined with the first sulphide precipitate and treated according to § 2.

---

[1] If the sulphides tend to run through the filter (*colloidal suspension*), a filter is used, that is washed with a 2 to 3% solution of ammonium nitrate, and the sulphides are washed with hydrogen sulphide water containing 2 to 3% ammonium nitrate. In cases of persistent difficulty, five grams of ammonium nitrate are added to the solution in which the sulphides are suspended.

2. The precipitated and washed sulphides are transferred to a porcelain dish and boiled, two or three minutes, with about ten volumes of *diluted* nitric acid (1 volume of dilute nitric acid of the laboratory (6-molar) is diluted with 2 volumes of water). The solution (S) is cooled, diluted and filtered from the residue (R), and reserved for analysis according to IV.

3. The residue[1] (R) is heated with dilute hydrochloric acid and a little potassium chlorate.[2] A portion of the diluted solution is tested with an excess of clear stannous chloride solution: a white precipitate (HgCl) or a gray one (Hg) shows **mercury**. Evaporate another portion of the solution under a hood in a porcelain dish and heat the residue gently to remove $HgCl_2$ (*poison!*). Treat the residue with water and a drop of hydrochloric acid, and test the filtered solution with hydrogen sulphide for **cadmium** (yellow CdS, insoluble in ammonium sulphide).

IV. *Analysis of the Solution* (S) *for Lead, Bismuth, Copper and Cadmium*

1. To the solution (S) a little sulphuric acid is added, in order to test it for **lead**, if it has not been found before, to *remove it*, if it has been found. Evaporate the solution with the sulphuric acid, in a porcelain dish over a small flame, until fumes begin to come off. *Cool* the residue and treat it with water and a little dilute sulphuric acid and filter the solution *at once* from any white precipitate (presumably *lead* sulphate, but possibly a basic sulphate of bismuth) that may be left. The solution is analyzed according to § 2. If **lead** has not been identified before, the precipitate is

---

[1] **R** may contain S, HgS (black), $Hg_2S(NO_3)_2$ (white) and CdS, and, when obtained in a systematic analysis, also Au_2S_2, PtS_2 and metastannic acid.

[2] If it is desired to examine the residue (R) for **tin**, the residue is treated, in a porcelain dish, with 10–40 c.c. saturated bromine water; the covered dish is warmed slightly for 5–10 minutes and its contents frequently stirred. The mixture is boiled to expel the bromine, the solution is cooled and filtered, and tested for **mercury** with stannous chloride. Metastannic acid is not dissolved by bromine water and would remain as an undissolved residue in the treatment. Such a residue is warmed gently with 2 c.c. ammonium sulphide solution, and the filtered solution is united with the main ammonium sulphide solution of the arsenic group, obtained in systematic analysis. (A. A. Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 171 (1907).) In regard to the examination of the residue (R) for **gold** and **platinum**, *vide* the same authors, *ibid.*

covered with potassium chromate solution, and the mixture warmed — the less soluble lead chromate would thereby be formed; a moderate excess of sodium hydroxide is added to the precipitate, the liquid is filtered and acidified with acetic acid. A yellow precipitate would be **lead** chromate.

2. The filtrate from the lead sulphate is still to be tested for *bismuth, cadmium and copper*. An excess of ammonium hydroxide is added to the solution. A precipitate is collected and tested as follows and the filtrate reserved for examination according to §§ 3 and 4: some of the precipitate (or, in the case of a trace, the whole precipitate, with the filter) is placed on a large watch crystal, or in a beaker, and stirred with a drop of hydrochloric acid carried to it by means of a glass rod. The watch glass or beaker is then filled with water. A white precipitate, (BiO)Cl, suspended in the water, proves the presence of **bismuth** (§ 3, p. 47). The original precipitate may also be treated with a solution of sodium stannite. If **bismuth** is present, a dark precipitate will appear (§ 4, p. 47). Unless one of these tests is obtained, the presence of bismuth has not been demonstrated.

3. If the ammoniacal solution, obtained in § 2, is blue, **copper** is present. To confirm, or to detect a trace of, **copper,** part of the solution is acidified with acetic acid and treated with two drops of potassium ferrocyanide solution (p. 46). Even a faint pink tint indicates **copper.**[1]

4. In the presence of copper, test the ammoniacal filtrate (§ 2) for **cadmium**[2] by adding potassium cyanide to it, until any color is discharged; a few *drops* excess of cyanide, and then hydrogen sulphide or ammonium sulphide are added. A yellow, or yellowish, precipitate would show the presence of **cadmium.** In the absence of copper, the treatment with potassium cyanide is omitted. Frequently the cadmium sulphide is discolored by traces of a black sulphide. If the color of the precipitate makes the presence of cadmium doubtful, the precipitate is washed and then it may be warmed with hydrochloric acid and the solution tested with the spectroscope (*Cadmium-ion,* § 3, p. 47); or the precipitate is boiled with three or four cubic centimeters of dilute sulphuric acid, the solution is filtered, diluted, made neutral with ammonium

---

[1] Cadmium ferrocyanide is a white precipitate and it reduces, if present, the intensity of the color of the copper salt. [2] To avoid KCN see p. 149.

hydroxide, acidified with only a *drop* or two of acid (why?) and treated with hydrogen sulphide to reprecipitate any **cadmium** sulphide.

THE ARSENIC GROUP

Arsenic, Antimony, Tin. (*Gold and Platinum*)

Group Reactions. — 1. (*a*) Cover some arsenious oxide with water and add sodium hydroxide to the mixture and warm it. What is formed?

(*b*) Add an excess of hydrochloric acid to a mixture of arsenious oxide and water, and warm the mixture. What is formed? According to (*a*) and (*b*) arsenious hydroxide is both acid and base. *Its acid properties are more pronounced* and it is called arsenious *acid.* This is the characteristic feature of the arsenic group, *especially in the case of the higher oxides* (each metal forms two oxides, As_2O_3, As_2O_5; Sb_2O_3, Sb_2O_5; SnO, SnO_2; Au_2O, Au_2O_3; PtO, PtO_2). As far as the higher oxides are concerned we are dealing essentially with a *group of acid-forming oxides,* with subordinate base-forming properties. *This is the chief difference between the arsenic group and all the previous groups.*

2. (*a*) Dissolve some sodium stannate in water, add hydrochloric acid, until the precipitated stannic acid is redissolved as the chloride, and pass hydrogen sulphide into the solution. Collect the sulphide on a filter and wash it. Treat some of it with a solution of ammonium sulphide. What is formed (Chap. XIII)? Compare the result with that obtained in 1 (*a*).

(*b*) Treat a solution of sodium sulpho-stannate with an excess of hydrochloric acid. Note the gas that is given off. What is the precipitate? What unstable acid is first liberated? Do you know an unstable oxygen acid that behaves in a similar manner?

Arsenic, antimonic, auric and platinic sulphides show the same behavior as is shown by stannic sulphide in (*a*) and (*b*), and *this behavior is characteristic of the group and is used to separate the group from the copper group.* Is the difference a chemical or a physical one?

3. (*a*) Add an excess of sodium hydroxide to a solution of stannous chloride. Has stannous hydroxide acid properties? Has it basic properties?

(*b*) Add ammonium hydroxide in excess to a solution of stannous chloride. Explain the difference in the results of (*a*) and (*b*). Can stannous hydroxide be a strong acid?

(*c*) Pass hydrogen sulphide into a solution of stannous chloride. Bring the precipitate on a filter (note its color) and treat part of it with colorless ammonium sulphide. In contrast to stannic sulphide (2 (*a*)), the precipitate hardly dissolves (compare the result with the behavior of the hydroxide in 3 (*b*)). Add to the mixture some pulverized roll sulphur and warm the mixture. Add an excess of hydrochloric acid to the solution obtained. What is the yellow precipitate? Explain the action of the sulphur.

As a rule the sulphur is dissolved in the ammonium sulphide before the latter is used, and so-called " yellow " ammonium sulphide, containing persulphides $(NH_4)_2S_x$, is used, already prepared. This dissolves the lower sulphides as well as the higher sulphides of the group, sulphurizing the lower ones. Which are the *stronger acid-forming* sulphides and oxides, the lower or the higher ones in the group?

Ions of Arsenic: Arsenious, As^{+++}; *Arsenic,* As^{+++++}; *Arsenite,* $AsO_3^{\equiv}$; *Arseniate,* $AsO_4^{\equiv}$

1. See 1 under *Group Reactions* (p. 52) in regard to the behavior of arsenious acid.

(*a*) Pass hydrogen sulphide into the hydrochloric acid solution of some arsenious acid. Note the color of the precipitate and note whether the latter forms *at once*. Give the equations.

(*b*) Pass hydrogen sulphide through 15–20 c.c. of an aqueous solution of arsenious acid: pour the resulting colloidal suspension of arsenious sulphide on a filter. Add to 5 c.c. of the suspension four or five drops of hydrochloric acid, and to another 5 c.c. add a few drops of ammonium chloride or nitrate solution (see Chap. VII).

2. (*a*) Add a small excess of dilute hydrochloric acid to a solution of potassium arseniate, to prepare a solution of arsenic acid, (H_3AsO_4), and pass hydrogen sulphide into the *cold* solution. Compare the result with 1 (*a*).

(*b*) Now heat the solution and continue the treatment of the hot solution with hydrogen sulphide for some time. Collect the precipitate on a filter, wash it and then treat it with ammonium hydroxide. What is left on the filter? Acidify the filtrate with hydrochloric acid. What is the action of hydrogen sulphide on arsenic acid under these conditions? (Chapter XIII.) Give the equations.

(*c*) Add to a solution of potassium arseniate concentrated hydrochloric acid to an acid reaction and then add a further excess of two volumes of the concentrated acid and pass hydrogen sulphide into this solution in the cold. After some time dilute the mixture somewhat and collect the precipitate. Treat it with an excess of ammonium hydroxide. It should all dissolve. What is the action of hydrogen sulphide on arsenic acid under these conditions? Give the equations. What do the experiments (*a*) and (*c*) suggest in regard to faint basic properties of arsenic acid and the formation of a quinquivalent arsenic ion in (*c*) (*cf.* Chap. XIII)?

The difficulty in precipitating arsenic sulphide in the cold, under the conditions [in (*a*)] used *for all other sulphides* of this and the previous group, is characteristic for *arsenic acid* (H_3AsO_4) and is due to its being the most *pronounced acid* and the least basic of all the hydroxides. *This fact must be always borne in mind in testing for arsenic, as even large quantities of the poisonous element may otherwise be overlooked.*

3. Add to potassium arsenite and arseniate solutions:

(*a*) Silver nitrate. Note the colors of the salts Ag_3AsO_3 and Ag_3AsO_4. They distinguish arsenites from arseniates.

(*b*) Ammonium nitrate, magnesium nitrate and ammonium hydroxide (use Magnesium Nitrate Mixture, see p. 146).

(*c*) Acidify with nitric acid 1. c.c. of each of the M/10 solutions, add the acid solutions to separate portions of "ammonium molybdate solution" (20 c.c. of the *nitric acid solution*[1]), and heat the mixtures to boiling. *Arsenic acid* forms a characteristic yellow precipitate, ammonium arsenomolybdate, $(NH_4)_3AsO_4$, 12 MoO_3.[2] (See Chap. XVI, the chemistry of the analogous phosphomolybdate.) A *large excess* of the molybdate solution is required.

4. (*a*) Prepare a glass tube four inches long and drawn out to a narrow, sealed point, at one end. Place a very *little* arsenious

---

[1] If an "ammonium molybdate solution without nitric acid" is used, add 10 c.c. of dilute nitric acid and about a gram of ammonium nitrate to 10 c.c. of the reagent before making the test.

[2] Kehrmann, *Z. anorg. Chem.*, 7, 420.

oxide in the narrow point and a piece of charcoal in front of it; heat the charcoal first to redness and let the heat spread very slowly towards the oxide, but keep the front half of the tube cold. What is the silver-gray sublimate that is formed? Explain the reaction and give its equation.

(*b*) Prepare a similar tube, but blown out to a small bulb at one end. Mix a little arsenic sulphide, dry sodium *carbonate* and dry potassium cyanide (care!) in a mortar and heat a little of the mixture in the bulb of the tube. What is the sublimate? (Difference from antimony.) For what purpose is the potassium cyanide used? Give the equation.

(*c*) Heat a *very* small amount of arsenious oxide, mixed with sodium carbonate, in the reducing flame of the blowpipe on charcoal and note the garlic-like odor of the arsenic. (Poison!)

(*d*) Read Fresenius, p. 284, on the Marsh test for arsenic. Students may make the test under the guidance of the assistant or may leave it to an advanced course.

(*a*), (*b*), (*c*) or (*d*) may be used as sensitive characteristic tests for arsenic, the Marsh test being the best, but the longest.

Ions of Antimony: Antimonous, Sb^{+++}; *Antimonic,* Sb^{+++++}; *Metantimonite,* SbO_2^-; *Antimonate,* $SbO_4^{\equiv}$, *Pyroantimonate,* $Sb_2O_7^{==}$

1. (*a*) Add to a solution of antimonous chloride, $SbCl_3$, an excess of sodium hydroxide. What is formed?

(*b*) Add to 1 or 2 c.c. of a solution of potassium pyroantimonate, $K_2H_2Sb_2O_7$, an excess of hydrochloric acid. What is formed?

What character of antimonous hydroxide and of antimonic acid is revealed in (*a*) and (*b*)?

(*c*) Recall the properties of $Na_2H_2Sb_2O_7$ (§ 6, p. 4).

2. Add antimonous chloride to a large excess of water. Recall what other metal chloride shows a similar behavior. Let the precipitate subside, decant the liquid, and add a solution of tartaric acid to the precipitate (difference from what similar precipitate?). (See Chapter XII.)

3. (*a*) Add to a solution of antimonous chloride a steel nail and enough hydrochloric acid to produce a vigorous evolution of hydrogen when the mixture is warmed. The black precipitate of metallic antimony is a *characteristic test for antimony* (difference from *tin*).

(*b*) Place a small piece of pure tin on a piece of platinum foil in a porcelain dish, and add, to it, a little hydrochloric acid and a drop of the solution of antimonous chloride. A black precipitate is produced on the platinum (*characteristic test for antimony*).

Express, in an equation, the reduction of antimonous chloride by iron. Judging by the relative positions of iron, tin, hydrogen and antimony in the table of solution-tensions (Chap. XV), should iron precipitate antimony or tin more readily from solutions of their chlorides in the presence of hydrochloric acid?

4. Pass hydrogen sulphide into a solution of antimonous chloride; note the color of the precipitated Sb_2S_3; the pentasulphide, Sb_2S_5, has the same color (*characteristic test for antimony*). Treat some of the sulphide with warm concentrated hydrochloric acid (difference from *arsenic* sulphides).

5. (*a*) Add an excess of hydrochloric acid to 1 or 2 c.c. of potassium pyroantimonate solution to prepare a solution of $SbCl_5$, and add a few drops of potassium iodide solution to it (difference of Sb^{+++++} from Sb^{+++}). Give the equation for the action, in terms of the electric theory of oxidation and reduction.

(*b*) Add to a solution (1 c.c.) of antimonous chloride enough potassium hydroxide solution to redissolve the precipitated hydroxide, thus forming potassium antimonite. Add to 2 or 3 c.c. of silver nitrate solution 2 or 3 c.c. of concentrated ammonia, and then add a few drops of the antimonite solution to the ammoniacal silver solution. If a white precipitate (AgCl) or a brown one (Ag_2O) is formed, add a little more ammonia solution to redissolve them; a *black precipitate* of silver indicates the presence of antimonite (difference of Sb^{+++} from Sb^{+++++}).

6. Heat a mixture of antimonous oxide, sodium carbonate and potassium cyanide in the reducing flame of the blowpipe. Antimony forms very brittle particles. Note the peculiar oxidation of the metal.

Ions of Tin: Stannous, Sn^{++}, *Stannic*, Sn^{++++}; *Stannite*, $SnO_2^{=}$; *Stannate*, $SnO_3^{=}$

1. (*a*) Are stannous hydroxide and stannic acid amphoteric in character? (See 2 (*a*) and 3 (*a*) p. 52.)

(*b*) Warm a small piece of tin with concentrated nitric acid. The white powder, known as *metastannic acid*, is insoluble in nitric acid and very difficultly soluble in hydrochloric acid, resembling

silicic acid in this behavior. It may, however, be dissolved by prolonged treatment with hot concentrated hydrochloric acid or, more easily, by boiling concentrated sulphuric acid (difference from *silicic acid*).

(*c*) Wash the precipitate with water, dry it and heat a little of it in a metaphosphate bead. Does it dissolve? (Resemblance to silicic acid.)

2. (*a*) Add stannous chloride to a solution of mercuric chloride, using the stannous chloride, finally, in excess: mercurous chloride and then mercury are precipitated (*characteristic test for stannous-ion*[1]). Express the two stages of the action, in two equations, in terms of the electric theory of oxidation and reduction. The first stage of the action, the formation and precipitation of mercurous chloride, is in itself a characteristic test[1] for the stannous-ion and the second action is a further characteristic test[1] for it. With small quantities of stannous-ion only the first stage is observed.

(*b*) Add a few drops of stannic chloride solution to a mercuric chloride solution. Then treat a little stannic chloride solution with a steel nail or two and some hydrochloric acid, for a few minutes, decant the solution, dilute it and add it to some mercuric chloride. (Applied in this way, the action studied in (*a*) may be used to find *tin* also when it is present in the form of the *stannic-ion*).

According to (*a*) and (*b*), stannic-ion is reduced to stannous-ion and not to tin, by iron in the presence of hydrochloric acid (*difference from antimony*). How does the presence of hydrochloride acid affect the action of iron on stannous-ion? (See the position of tin and hydrogen in the table of solution tensions, Chap. XV.)

(*c*) *Zinc*, which has a *much higher solution tension* than iron (see the table), reduces stannous-ion to tin, even in the presence of hydrochloric acid. Judged by the table of solution tensions, would the tin remain unaffected after all the zinc has been dissolved, or would it liberate hydrogen from hydrochloric acid and be redissolved as stannous chloride ($Sn\downarrow + 2\,H^+ \rightleftarrows Sn^{++} + H_2\uparrow$)? To answer this question, treat 1 or 2 drops of stannous chloride solution, in a small porcelain dish, with a fragment of zinc and 2 or 3 c.c. of hydrochloric acid; note the spongy appearance of the tin, resulting from the *occlusion* of *hydrogen.* When all the zinc has disappeared, let the action of the acid on the tin go on for some time; the tin will redissolve. What does the result of this experiment indicate in regard to the question whether, when tin is precipitated by zinc in the presence of hydrochloric acid, Sn, Sn^{++}, H_2 and H^+ are *in equilibrium* in the system, as a whole, or whether the precipitation of tin, together with hydrogen, is not the result of the intense local action[1] of the zinc?

---

[1] In the absence of *other reducing agents*.

If zinc or tin, in contact with a piece of platinum foil, is covered with an acid solution of stannous or stannic chloride, the platinum is not coated black (difference from *antimony*).

3. Stannous and stannic sulphides, like antimonous and antimonic sulphides, are soluble in warm, concentrated hydrochloric acid (difference from *arsenic* suphides).

Platinum Ions: Platinous, Pt^{++}, *Platinic* Pt^{++++}, *Platinite,* $PtO_2^{=}$, *Platinate,* $PtO_3^{=}$; *and Gold Ions: Aurous,* Au^+, *Auric,* Au^{+++}; *Aurate,* AuO_2^-

NOTE: *Put all platinum and gold residues into the appropriate bottles on the side shelf.*

1. (*a*) Add a drop of chloroplatinic acid, H_2PtCl_6, solution to potassium chloride solution. What is the composition of the precipitate? From what ions is it formed? Read Remsen's *Advanced General Chemistry,* pp. 465, 614, 729, on chloro-acids, chlorauric and chloroplatinic acids.

(*b*) Add a drop of silver nitrate solution to a drop of chloroplatinic acid solution; then add a few drops of ammonia solution. Is the precipitate[2] silver chloroplatinate or silver chloride?

---

[1] When an electric current is passed through a solution of cupric sulphate and nitric acid and the current used is small in proportion to the surface of the cathode, only copper is deposited, copper having a much smaller solution-tension than hydrogen; the deposit of copper is dense and compact. But if a current is used *that is so heavy that cupric ions cannot reach the cathode fast enough to absorb the electrons discharged, then hydrogen as well as copper* is liberated and the copper is made loose and spongy. With the same heavy current a dense deposit of copper may be secured, without the formation of any hydrogen, if, *by extremely vigorous stirring of the solution,* the cathode is kept supplied with cupric-ion (principle of the rotating (stirring) anode in electrolysis, Edgar F. Smith, *Electroanalysis* (1907).

[2] *Cf.* Jorgensen, *J prakt. Chem.,* (2) **16,** 349 (1877).

(*c*) Pass hydrogen sulphide into a mixture of a drop or two of chloroplatinic acid and a little water. Does a sulphide form readily? Heat the mixture. Does chloroplatinic acid give any positive ions of platinum at all? On the basis of (*a*), (*b*), (*c*), give a complete statement of the ionization of chloroplatinic acid and indicate the chief ions formed. Can $PtCl_6^=$ be considered a complex ion? (Chapter XIII.)

Treat the sulphide, obtained in 1 (*c*), with a few drops of ammonium sulphide solution. It will ultimately dissolve to give ammonium sulphoplatinate (see p. 52, 2). What are the ions of the latter salt? Can $PtS_3^=$ be considered a complex ion? (Chapter XIII.)

(*d*) Read in Remsen, *loc. cit.* p. 730, on the platinates and the platinocyanide salts (*e.g.* $K_2Pt(CN)_4$). What four classes of *negative* ions does platinum enter into? Can they all be considered to be complex ions? Are there complex ions of elements with oxygen? Is there any essential difference between the four classes?

2. (*a*) To two or three drops of gold chloride solution (storeroom) add a drop of hydrochloric acid and saturate the solution with hydrogen sulphide; add a drop of ammonium hydroxide solution and some yellow ammonium sulphide to the precipitate.

(*b*) Repeat (*a*), but treat the sulphide with a few drops of potassium cyanide solution. Why does the cyanide dissolve the gold sulphide? Electrolyze this solution, for a few minutes, in a little cell, and note *on which pole* gold is deposited (Instructor). Is this result consistent with the solubility of gold sulphide in the cyanide?

3. (*a*) Evaporate a drop, each, of the solutions of chloroplatinic acid and gold chloride on porcelain lids and heat the residues to redness. Give the equations for the reactions. Add to the metallic stains a drop of concentrated nitric acid. Then add to this a drop of concentrated hydrochloric acid, to produce aqua regia.

(*b*) Heat a little precipitated silver chloride, in like fashion, on a porcelain lid. Is metallic silver formed? What do (*a*) and (*b*) show as to the relative stability of the metal chlorides?

4. (*a*) Mix some potassium chloroplatinate (from 1 (*a*)) with a little dry sodium carbonate and heat the mixture, in the loop of a platinum wire, in the blowpipe flame. Treat the mass, in

an *agate* mortar (storeroom), with a little water and polish the platinum powder. Why is the platinum obtained as a powder?

(*b*) Heat a little gold sulphide, with or without sodium carbonate, in a cavity of a piece of charcoal, before the blowpipe. Polish the gold in an ordinary mortar and note what minute quantities can be seen in this way.

5. Treat a drop of chloroplatinic acid and gold chloride solutions, each separately, with water and

(*a*) Ferrous sulphate and a drop of hydrochloric acid.

(*b*) Oxalic acid (heat). Chlorides, in excess, must be avoided.

(*c*) Potassium iodide solution.

6. Add to a drop of gold chloride solution, diluted with 10 c.c. of water, slowly, a stannous chloride solution, prepared from a drop of the reagent in 10 c.c. of water. The resulting color is the color of *colloidal gold* (Chapter VII) and is called "Cassius purple." Allow the precipitate to settle, or collect it on a small filter. Wash the precipitate twice with water and then cover it with some ammonium hydroxide solution: it will form a purple, colloidal suspension of gold, which may remain clear for weeks (Chapter VII).

Characteristics of the Arsenic Group. The higher oxides and sulphides of the metals are pronounced acid-forming compounds. The sulphides combine readily with sodium and ammonium sulphides to form soluble alkali salts of sulpho-acids (*difference from all the previous groups*). The sulphides are so insoluble that they are precipitated by hydrogen sulphide even in the presence of a small amount of a strong acid (*difference from the zinc, aluminium, alkaline earth and alkali groups*).

Gold and platinum, the so-called "noble metals," differ from the other metals of the group by the readiness with which their compounds are reduced and the metals formed. Advantage may be taken of this property in separating them from the remaining metals of this group and from the other groups.[1]

ANALYSIS OF THE ARSENIC GROUP[2]

Ask for an "unknown" solution of the arsenic group and analyze it according to method A or B.

---

[1] *Cf.* Fresenius, p. 303.

[2] Platinum and gold are not included here, but are included in Systematic Analysis, Part IV, p. 105.

METHOD A

I. *Precipitation and Separation of the Sulphides*

1. Use 10 c.c. of the "unknown." (*a*) If it has an *acid* reaction, dilute the solution to 40–50 c.c. and determine the approximate degree of acidity of the mixture by the methyl violet test (p. 31): if a yellow or a yellow-green tint is produced, the acid is sufficiently strong — proceed to § 2. If a blue or a blue-green tint is produced, add hydrochloric gradually to the solution (an undue excess is to be avoided), until the strength desired is reached. Then proceed with the solution according to § 2.

(*b*) If the "unknown" has an *alkaline* reaction, add hydrochloric acid to it: if a precipitate is produced (*e.g.* antimonic or stannic acid), add sufficient acid to redissolve the precipitate, avoiding the use of an unduly large excess. Whether a precipitate has formed or not, dilute the acid solution to 40–50 c.c. and test the solution with methyl violet, proceeding as directed in (*a*).

2. Pass hydrogen sulphide into the cold acid solution to saturation, filter the solution from the precipitate (using the filter pump) and then pass hydrogen sulphide, for fifteen minutes, into the filtrate, at 90°, to insure the precipitation of arsenic. (Which form of arsenic is precipitated with difficulty as the sulphide, the arsenious or the arsenic?) Add any precipitate, thus formed, to the previous precipitate and wash the combined precipitates with ammonium chloride solution. Dilute the filtrate, including the washings, to 100–150 c.c. and test the acidity of the solution with methyl violet: if a blue or a blue-green tint is produced, pass hydrogen sulphide into the cold solution to determine whether any sulphide (*e.g.* SnS, Sb_2S_3) was not precipitated by the previous treatment with hydrogen sulphide, as the result of the presence of too great a concentration of acid (Chap. XI). If a yellow or a yellow-green tint is produced in the methyl violet test of the diluted filtrate (measuring 100–150 c.c.), too much acid is present to allow the precipitation of all the sulphides; the solution is rapidly evaporated to dryness, in a shallow dish, the residue is dissolved in 4 c.c. of hydrochloric acid, the solution diluted to 100 c.c. with water and tested, in the cold, with hydrogen sulphide. The combined sulphides are collected, drained on a filter pump, transferred to a beaker and warmed with 3 to 5 c.c. of concentrated hydrochloric acid, as long as there is a *brisk* evolution of hydrogen

sulphide. **Antimony** and **tin** sulphides dissolve (solution (S)); the sulphides of **arsenic** remain practically completely undissolved, with sulphur, which is always present. The solution (S) is diluted with an equal volume of water and filtered from the residue (**R**).

II. *Examination of the Residue* (**R**) *for Arsenic*

2. The residue (**R**) should be tested for **arsenic** in two ways. First, a small portion is boiled with 3 c.c. of concentrated nitric acid as long as brown fumes form, to convert any arsenic into arsenic acid; a few drops of this solution are heated, to boiling, with 10 c.c. of molybdate (nitric acid) solution (see Arsenic, 3 (*c*)). A *yellow* precipitate of ammonium arsenomolybdate proves the presence of **arsenic.** If no yellow precipitate is formed, add a larger portion of the nitric acid solution of the residue (**R**) to the molybdate solution and boil the mixture again. (The precipitation requires a *large excess* of the reagent and so the test is first made with *small quantities of the substance.*) A second small portion of the residue (**R**) is treated with a little ammonia, the solution is filtered and evaporated to dryness, in a porcelain dish over a very small flame, after the addition of a little sodium carbonate. The dried residue is tested with potassium cyanide (care!) in a tube, according to p. 55, 4 (*b*). A black sublimate indicates **arsenic.**

III. *Examination of the Solution* (**S**) *for Tin and Antimony*

3. The solution (S) is boiled to remove every trace of hydrogen sulphide test; half of it is then treated with a steel nail or two. A precipitate of black flakes indicates **antimony.** The **tin** remains in solution as stannous chloride, and, after the solution is diluted, is identified by means of mercuric chloride (p. 57, § 2 (*a*)). As steel gives a little carbon, which may be mistaken for *antimony,* the latter is best fully identified by converting it into the orange sulphide. The black precipitate is collected and warmed with some tartaric acid and a drop or two of dilute nitric acid; the solution is diluted and saturated with hydrogen sulphide. In place of this confirmation test for antimony, a small portion of the solution (S) may be tested for **antimony,** according to p. 55, 3 (*b*), with tin and platinum foil.

METHOD B

1. Test a few *drops* of the original unknown for **arsenic, antimony** and **tin** as follows: (Hofmann's modification of Marsh's test.) (Use *the hoods.*) Fit a 250-c.c. flask with a thistle (safety) tube and a delivery tube, connect the latter with a U-tube half-filled with glass beads (storeroom). The exit of the U-tube is connected with a bent glass tube dipping into a long test tube. Moisten the beads with lead acetate solution, generate hydrogen in the flask from some pure zinc and dilute hydrochloric acid, and test whether all connections are air-tight, by closing the exit for a moment and observing whether the acid rises high in the thistle tube. If the connections are good, pour 10 c.c. of silver nitrate solution into the test tube, put *one drop* of the unknown solution into the thistle tube, rinse it into the generator and let the gases pass through the silver nitrate for several minutes. (They are poisonous gases! Care!) A second and a third drop may be used, if it seems necessary. Disconnect the generator and stop the evolution of any arsine, by pouring the acid off the zinc (hood-sink) and rinsing the zinc with water. Reserve the zinc to test it according to § 4 for a deposit of **tin.**

2. If **arsenic** is present in the unknown, arsine is formed in the hydrogen generator. It is oxidized by silver nitrate to arsenious acid, which remains in solution, together with the excess of silver nitrate and with nitric acid formed in the action. Stibine, which is formed if antimony is present in the unknown, forms insoluble silver antimonide, $SbAg_3$, which would be found in the precipitate, together with metallic silver, formed by the action of arsine on silver nitrate.

Filter the silver nitrate solution from any precipitate formed, add 2 or 3 c.c. of ammonium nitrate[1] solution to the filtrate, and cover the mixture, in a test tube, with a *zone* of diluted ammonia solution by letting 3 to 4 c.c. of the latter flow slowly, from a pipette, down the side of the test tube, while the test tube is held in an inclined position. At the neutral junction between the acid and alkaline zones, *yellow silver arsenite* will show if **arsenic** is present.

---

[1] The ammonium nitrate is intended to prevent the formation of a brown zone of silver oxide, in the subsequent test with ammonia: in the absence of arsenious acid and of nitric acid in the solution, silver oxide would be formed.

The neutral zone is best observed against a dull white background and may be enlarged by a *very gentle* swaying of the test tube.

The action of silver nitrate on arsine, by which the latter is oxidized to arsenious acid, may be expressed as follows;

$$\mathrm{As}^{\equiv}\mathrm{H}_3^{+} + 6\,\mathrm{Ag}^{+} + (6\,\mathrm{NO}_3^{-}) \rightarrow \mathrm{As}^{+++} + 3\,\mathrm{H}^{+} + 6\,\mathrm{Ag}\downarrow + (6\,\mathrm{NO}_3^{-}). \qquad \text{(1)[1]}$$

$$\mathrm{As}^{+++} + (3\,\mathrm{NO}_3^{-}) + 3\,\mathrm{HOH} \leftrightarrows 3\,\mathrm{H}^{+} + (3\,\mathrm{NO}_3^{-}) + \mathrm{As(OH)}_3. \qquad \text{(2)[2]}$$

3. Any *precipitate*, formed in the silver nitrate solution (§ 1) and collected according to § 2, is examined for **antimony** as follows: it is washed with 20 c.c. of boiling water and then boiled with a little tartaric acid, which dissolves any antimony present (see p. 55, § 2). The liquid is filtered and tested with hydrogen sulphide for **antimony** (orange sulphide).

The action of silver nitrate on stibine may be expressed as follows:

$$\mathrm{SbH}_3 + 3\,\mathrm{Ag}^{+} + (3\,\mathrm{NO}_3^{-}) \rightleftarrows \mathrm{SbAg}_3\downarrow + 3\,\mathrm{H}^{+} + (3\,\mathrm{NO}_3^{-}). \qquad (3)$$

What analogy does this bear to the action of silver nitrate on hydrogen sulphide? Is stibine possibly ionizable to a certain degree? Does hydrogen sulphide show any actions resembling, in part, that of arsine (equation (1) or (1′) above) as well?

4. Any **tin** in the original unknown would be deposited on the zinc in the generating flask. The zinc and any adhering tin may be dissolved completely in warm hydrochloric acid and the solution tested for stannous chloride by means of mercuric chloride; a white precipitate of mercurous chloride or a gray precipitate of mercury would indicate the presence of **tin**.

By a study of the "group characteristics" (pp. 5, 17, 29, 35, 48 and 60) and of the table of groups (Chap. IX), work out a scheme of analysis for separating the groups of metal ions from one another. Show your method to an instructor and ask for an "unknown" containing a representative of each group. Separate the groups according to the approved scheme, analyzing each group (precipitate) according to the appropriate group analysis (pp. 5, 17, 35, 48 and 60), until the group representative is found.

---

[1] See Chapters XIV and XV in regard to oxidations through the transfer of the positive charges of silver ions. AsH_3 is probably slightly ionizable according to $\mathrm{AsH}_3 \rightleftarrows \mathrm{As}^{\equiv} + 3\,\mathrm{H}^{+}$, and we have, probably, simply,

$$\mathrm{As}^{\equiv} + 6\,\mathrm{Ag}^{+} \rightarrow \mathrm{As}^{+++} + 6\,\mathrm{Ag}\downarrow. \qquad (1')$$

[2] This action represents simply an hydrolysis of arsenious nitrate. Why should it be hydrolyzed?

B. REACTIONS OF THE ACID IONS

GROUPS OF ACID IONS[1]

I. *Group of Ions of Amphoteric Acids and Related Acids:* $AsO_4^{\equiv}$; $AsO_3^{\equiv}$; $SbO_4^{\equiv}$; SbO_2^{-}; $SnO_3^{=}$; $SnO_2^{=}$; $PtO_3^{=}$; AuO_2^{-}; AlO_2^{-}; $ZnO_2^{=}$; $PbO_2^{=}$; CrO_2^{-}; $CrO_4^{=}$; $Cr_2O_7^{=}$; MnO_4^{-}

The whole arsenic group of metals form hydroxides, as has been seen, which are amphoteric, and the higher hydroxides are pronounced *acids* (p. 52). Aluminium, chromium, zinc and lead hydroxides were also found to be amphoteric, although *primarily bases.* All of these amphoteric *acids,* as a result of their basic character, are found in the course of systematic analysis for *metal ions,* and, if that has been carried out with care, it should be unnecessary to make any further examination for them. The problem of determining whether an amphoteric compound is originally present as a basic or acid component of an unknown is discussed under Systematic Analysis, Part IV, p. 116.

In addition to these amphoteric acids, chromic and permanganic acids reveal themselves in the analysis for metal ions, as a result of their *reduction* by hydrogen sulphide to *chromium* and *manganous* ions. They are therefore included in this group.

II. *Carbonate Group:* $CO_3^{=}$; $SiO_3^{=}$; $S^{=}$; HS^{-}; (NO_2^{-}, $SO_3^{=}$ and other less common anions)[2]

Add hydrochloric acid to sodium carbonate; to ferrous sulphide.[3] Acids which are liberated by hydrochloric acid as *gases* (or form gaseous decomposition products), and acids which are readily converted into free *solid acids, insoluble* in excess of hydrochloric acid, are: carbonic acid, which easily forms gaseous carbon dioxide; hydrogen sulphide; hydrocyanic acid; and silicic acid, which is easily converted into an " insoluble silicic acid " (see p. 70). Other, less common, acids belonging to this group are nitrous and sulphurous acids and a long series of sulpho-acids (*e.g.* sulphostannic acid, H_2SnS_3, pp. 52 and 93), and of cyanide acids (*e.g.* argenticyanic acid, $HAg(CN)_2$; pp. 43 and 93). Hydrocyanic acid is found also in the chloride group and treated best with the acids of that group; hydrogen sulphide is also found in the chloride group, and may be considered in connection with either group.

---

[1] See Chapter XVI.

[2] Bracketed anions are not included in the systematic analysis given in this book.

[3] Hydrogen sulphide is not always liberated so easily from its salts. Its behavior will be studied in detail below.

III. *Sulphate Group:* $SO_4^=$; $(SiF_6^=)$

(*a*) Add to 5 c.c. of sodium sulphate solution a few drops of $BaCl_2$ solution, then add 1 or 2 c.c. of hydrochloric acid to the mixture. *Barium sulphate, insoluble in dilute acid,* is precipitated. (*b*) Add a few drops of $BaCl_2$ solution to 5 c.c. of sodium phosphate solution and then add 1 or 2 c.c. of hydrochloric acid to the mixture: the precipitate of barium phosphate is found to be *readily soluble* in dilute acid. Barium sulphate is the only common barium salt which is insoluble in dilute hydrochloric or nitric acid. The barium salt of a less common acid, fluorosilicic acid, $BaSiF_6$, behaves in this respect as does $BaSO_4$.

IV. *Chloride Group:* Cl^-; Br^-; I^-; CN^-; CNS^-; $Fe(CN)_6^{==}$; $Fe(CN)_6^{\equiv}$; $S^=$; HS^-[1]

Add silver nitrate and then nitric acid to: (*a*) sodium chloride; (*b*) sodium phosphate. Silver bromide, iodide, cyanide, sulphide, sulpho-, ferro-, and ferricyanide are, like the chloride, almost insoluble in cold, dilute nitric acid.

Silver oxide, arsenite, arseniate, chromate, carbonate, oxalate, tartrate, silicate, borate, like the phosphate, are rather difficultly soluble in water, but readily soluble in nitric acid.

Silver nitrate, chlorate, fluoride, sulphate, permanganate, acetate, are easily to moderately soluble in water.

V. *Phosphate Group:* $PO_4^{\equiv}$; BO_2^-; $F_2^=$; $C_2O_4^=$

Phosphoric, boric, hydrofluoric and oxalic acids form barium (calcium and silver) salts[2] which are difficultly soluble in water, but readily soluble either in hydrochloric or nitric acid.

Barium (calcium and silver) salts of a number of acids, which are found in other groups, show a similar behavior (see Chap. XVI and the table of solubilities at the end of this book). Only those acid ions are named in the group, which are not found more conveniently in these other groups. Oxalate-ion may also be conveniently considered in the group of organic acid ions (VII); but it occasionally is found in connection with tests for the fluoride-ion and so is named in this group as well as in the group of organic acid ions.

---

[1] $S^=$ and HS^- belong also to the *carbonate group* and may be considered in either group.

[2] Silver fluoride is soluble in water.

VI. *Nitrate Group:* NO_3^-; ClO_3^-

The common salts of nitric acid and of chloric acid are soluble in water.[1]

VII. *Group of Organic Acid Ions: Oxalate,* $C_2O_4^{--}$; *Acetate,* $CH_3CO_2^-$; *Tartrate,* $(CHOH)_2(CO_2)_2^{--}$; *Benzoate,* $C_6H_5CO_2^-$; *Salicylate,* $C_6H_4OHCO_2^-$

The common organic acids may be conveniently classified together as a further group of acids; their presence or absence, as a group, may be readily ascertained. Only oxalic, acetic-tartaric, benzoic and salicylic acids, as typical representatives, are considered in this book. There are innumerable other organic acids.

I. GROUP OF AMPHOTERIC ACIDS AND RELATED ACIDS

Arseniate-ion, AsO_4^{---}, and *Arsenite-ion,* AsO_3^{---}. (See Arsenic, p. 53. The two acids are distinguished from each other according to p. 54, § 3 (*a*, *b* or *c*).)

Antimonate Ions, SbO_4^{---}, $Sb_2O_7^{----}$ etc., *Antimonite-ion,* SbO_2^-. (See Antimony, p. 55. Antimonites may be distinguished from antimonates according to p. 56, § 5*a*, *b*.)

Stannate-ion, SnO_3^{--}; *Stannite-ion,* SnO_2^{--}. (See Tin, p. 56. Stannites and stannates may be distinguished from each other according to p. 57, § 2*a*, *b*.)

Platinate-ion, PtO_3^{--}, *Aurate-ion,* AuO_2^-. (See Gold and Platinum, p. 58.)

Plumbite-ion, PbO_2^{--}. (See Lead, p. 44, § 1.)

Aluminate-ion, AlO_2^-, *Zincate-ion,* ZnO_2^{--}. (See Aluminium, p. 22, and Zinc, p. 34.)

Chromite-ion, CrO_2^-. (See Chromium, p. 25. Chromites are distinguished from chromates by the colors of the salts and by the reactions of chromic acid towards reducing reagents (H_2S,KI) and towards hydrogen peroxide (see below). Chromates, which contain no other color-producing element, are yellow or red.)

Chromic Acid, H_2CrO_4; *Chromate-ion,* CrO_4^{--}. *Dichromic Acid,* $H_2Cr_2O_7$; *Dichromate-ion,* $Cr_2O_7^{--}$

1. Treat potassium chromate with hydrochloric acid and hydrogen sulphide. To what is the change of color due? Write the

---

[1] Basic salts, like $(BiO)NO_3$, are occasionally difficultly soluble.

equation for the reaction from the electric point of view (Chapter XV).

2. (*a*) Add silver nitrate to potassium chromate.

(*b*) Dilute a mixture of 1 c.c. each of molar solutions of sodium chloride and potassium chromate to 10 c.c. and determine the relative solubility of the silver salts by adding silver nitrate solution, drop by drop, to the mixture, which must be shaken vigorously after the addition of each drop or two.

3. Add a little hydrochloric acid to a solution of potassium chromate and compare the color of the acidified solution with that of potassium dichromate. Add potassium hydroxide to a solution of potassium dichromate.

The first action of a strong acid on potassium chromate forms an acid chromate (corresponding to acid carbonates, such as $NaHCO_3$, acid phosphates, Na_2HPO_4, etc.), but the acid salt, or its ion $HCrO_4^-$, loses water spontaneously and goes over into a partial anhydride, the dichromate:[1] $2\ K_2CrO_4 + 2\ HCl \rightleftarrows 2\ KHCrO_4 + 2\ KCl$ and $2\ KHCrO_4 \leftrightarrows K_2Cr_2O_7 + H_2O$.

Note that the actions are reversible and state how the conditions of equilibrium would be affected by the addition of an alkali.

4. Prepare some hydrogen peroxide from barium peroxide and dilute hydrochloric or sulphuric acid. Add to a few cubic centimeters of water a drop or two of potassium dichromate solution, a drop of dilute hydrochloric acid and several cubic centimeters of ether; then add some of the hydrogen peroxide solution and shake the mixture. This is a characteristic and sensitive *test* for *chromic acid* and for hydrogen peroxide.[2]

Permanganic Acid, $HMnO_4$. *Permanganate-ion*, MnO_4^-

1. Examine the absorption spectrum of an extremely dilute (pale purple) solution of potassium permanganate by the method described on p. 24. Dilute the solution, if necessary, until the separate bands of the spectrum are well defined.

---

[1] The structure of the acid chromate is $KO(CrO_2)OH$, and the union of two molecules with loss of water, forming a partial anhydride, occurs according to:

$$KO(CrO_2)OH + HO(CrO_2)OK \rightleftarrows KO(CrO_2)O(CrO_2)OK + H_2O.$$

The dichromate-ion $HCrO_4^-$ would lose water in the same way.

[2] See Byers and Reid, *Am. Chem. J.* **32**, 503 (1904), in regard to the composition of the product. (Stud.)

5月2日[illegible]

Solutions of all permanganates show the same color and the same absorption spectrum.[1]

2. Pass hydrogen sulphide into a solution of potassium permanganate that has been acidified with sulphuric acid. The colorless solution formed contains manganous sulphate. Write the reaction equation in terms of the electric theory of oxidation and reduction (Chapter XV).

NOTE. Permanganates are such powerful oxidizing agents that care must be taken not to rub or heat them, in the dry state, with reducing agents.

II. THE CARBONATE GROUP

Carbonic Acid, H_2CO_3; *Carbonate-ion,* $CO_3^=$

Treat any carbonate with hydrochloric or nitric acid. Decant the evolved gas into a test tube containing several cubic centimeters of limewater, and then shake the latter, after closing the tube with the thumb.

For the detection of small quantities of carbonic acid by the limewater test, fit each of two test tubes with a double-bored stopper, with a glass tube, bent at right angles, reaching almost to the bottom of the test tubes, as well as with a short delivery tube, also bent at right angles. The first test tube is charged with the substance to be examined for the presence of a carbonate, its long tube is connected with a short calcium chloride tube, which is charged with soda-lime (intended to absorb CO_2 from the air current, used in the experiment), and its short delivery tube is connected with the long tube of the second test tube. The latter test tube is charged with a small volume of clear limewater and its short delivery tube is connected with the water-pump. When the apparatus is thus adjusted and charged, a little hydrochloric or nitric acid is added to the specimen under examination (in the first test tube) and a slow current of air is passed through the whole apparatus, by means of suction induced by the water-pump. The current is continued for several minutes.

Silicic Acids[2]

1. Heat a particle of glass or of sand in a metaphosphate bead and note the insoluble silica "skeleton." Recall the chemistry of the metaphosphate bead (p. 26). See p. 57, § 1 (*c*), for the similar behavior of stannic acid.

---

[1] Ostwald, *Z. phys. Chem.*, **9**, 579 (1892). In the presence of strongly colored metal ions, additional absorption bands and a slight variation of tint may be found in sufficiently concentrated solutions.

[2] See Smith's *General Inorganic Chemistry*, p. 524.

2. Prepare a solution of sodium silicate (1 gram in 10 c.c.) in water and test the solution as follows:

(*a*) Test the reaction of the solution with litmus paper. Then heat 2 c.c. of the solution and add dilute hydrochloric acid, drop by drop, to it until the reaction is slightly acid. As a rule, a part of the silicic acid separates out under these conditions in a gelatinous, insoluble form.

(*b*) Dilute 2 c.c. of the solution to 5 c.c. with water and add hydrochloric acid in excess to it. Then render it slightly alkaline with ammonium hydroxide solution. Compare the observed behavior of silicic acid with that of aluminium hydroxide under similar conditions (p. 23, § 4 *c*).

(*c*) To 2 c.c. of the solution, diluted to 5 c.c., add an excess of hydrochloric acid. Whether a precipitate is formed or not, evaporate the mixture to dryness on the steam bath, and then heat the dried residue 40 to 60 minutes longer on the steam bath or fifteen minutes at 120°. Add dilute hydrochloric acid to the residue and warm the mixture. The *insoluble residue* left is the so-called "insoluble silicic acid." This behavior gives us the most convenient *test for silicic acid.* The residue may be further identified as silicic acid according to § 1 or § 4.

3. Pulverize a piece of glass or of porcelain, mix the powder with equal parts of dry sodium and potassium carbonate and fuse the mixture in a small platinum dish (Instructor). Extract the mass with water, acidify the mixture with hydrochloric acid and proceed as directed in 2 (*c*).

4. Mix a little silica with some fluorspar and concentrated sulphuric acid, in a lead dish with a perforated lead cover, hold a drop of water in the loop of a platinum wire over the opening in the cover and warm the dish very gently. A *white deposit* (silicic acid) will form on the loop (difference from *stannic acid*).

Hydrofluoric acid forms with silicon dioxide, or with silicic acid, silicon tetrafluoride, which is a gas. The fluoride in turn is very easily decomposed by water, the action by which it is formed being largely reversible:

$$Si(OH)_4\downarrow + 2\,H_2F_2 \rightleftarrows SiF_4\uparrow + 4\,H_2O.$$

What does this reversible reaction suggest as to weak *basic* properties of silicic acid? Considering the reversible action, should the fluoride be prepared in the presence of much or little water? How would the fact that the fluoride is a gas affect the reversible process, if the action is allowed to proceed in an open space?

With an excess of hydrofluoric acid, SiF_4 combines to form fluorosilicic acid: $SiF_4 + H_2F_2 \leftrightarrows H_2SiF_6$. Fluorosilicic acid is stable in aqueous solution, whereas silicon tetrafluoride, as stated, is very easily decomposed. What does that behavior indicate as to the stability of the complex fluorosilicate ion, according to $SiF_6^{=} \rightleftarrows Si^{++++} + 3\ F_2^{=}$? (See Chap. XII, p. 237.)

As a result of the formation of fluorosilicic acid, the decomposition of the tetrafluoride by water involves only a part of the fluoride. We may combine the equations representing the two actions into a single equation as follows: $3\ SiF_4 \uparrow + 4\ H_2O \leftrightarrows Si(OH)_4 \downarrow + 2\ H_2SiF_6$.

Hydrogen Sulphide (*Hydrosulphuric Acid*), H_2S; *Hydrosulphide-ion*, HS^- *and Sulphide-ion*, $S^=$

1. Treat each of the following sulphides with dilute and concentrated hydrochloric acid and test, with a strip of filter paper moistened with ammoniacal silver nitrate or sodium plumbite (*test for hydrogen sulphide*), whether hydrogen sulphide is evolved: FeS; PbS; As_2S_3; HgS. Recall the behavior of the metal salts toward hydrogen sulphide in the presence of hydrochloric acid.

2. At the sealed end of a narrow glass tube put a mixture of mercuric sulphide and dry sodium carbonate, cover it with a layer of the carbonate, heat the latter first and then the mixture. Extract the cooled mass with water and test the filtrate for a sulphide according to 1.

3. Treat some sulphide with a little aqua regia. Boil the mixture, dilute it with a very large amount of water and add barium chloride. What is formed?

4. Add a drop of hydrogen sulphide water and some sodium hydroxide to sodium nitroprussiate. This is a very sensitive *test for hydrogen sulphide and the sulphide-ion.*

III. THE SULPHATE GROUP[1]

Sulphuric Acid, H_2SO_4; *Sulphate-ion*, $SO_4^=$

1. (*a*) Add barium chloride to sodium sulphate and then add a little dilute hydrochloric or nitric acid. Since all other ordinary barium salts[1] are soluble in dilute acid, *sulphate-ion can*

---

[1] *Barium fluorosilicate*, $BaSiF_6$, like barium sulphate, is insoluble in dilute acids. If a fluoride is present in a substance, fluorosilicic acid is liable to be formed in acid solutions in glass or porcelain vessels (see p. 70). A precipitate obtained according to 1 (*a*) is identified, in such a case, according to 2. $BaSiF_6$ treated with concentrated sulphuric acid, in a test tube of 2 to 3 c.c. capacity, forms SiF_4, which may be identified by means of a drop of water in the loop of a platinum wire held in the vapor.

chloride-ion can only be identified after the removal or destruction of the interfering acid ions.

2. Add some iodine, dissolved in an aqueous solution of potassium iodide, to the following reagents; repeat the tests with bromine water and then with chlorine water.

(*a*) A few drops of chloroform or carbon disulphide.[1] Note the colors of the chloroform or carbon disulphide layers. (Test for *iodine* and for *bromine.*)

(*b*) A starch solution. Note the color produced, if any. (Test for *iodine.*) (The starch solution is prepared by putting a *small* pinch of starch into a beaker full of boiling water and boiling the mixture a few minutes.)

Separation and Identification. 3. (*a*) Add 5 c.c. dilute sulphuric acid to 5 c.c. each of molar solutions of potassium chloride, bromide and iodide, and expose the acidified solutions, as well as the separate salt solutions, to the air for twenty-four hours. Which halogen acid is *oxidized* most easily? Is the salt of the same acid oxidized as easily as the acid, under the conditions of this experiment? Which of these three halogens has the smallest tendency to form its ion (see Chapter XIV)? The difference in this tendency, which *determines the ease with which the ion is oxidized to form the free halogen,* is used in recognizing these halogens in the presence of one another; *iodide-ion* is found according to 4 (*a*) or (*b*), *bromide-ion* according to 4 (*b*), *chloride-ion,* in the presence of iodide or bromide, according to 4 (*c*). An alternative method of detecting the three acids in the presence of one another is given in 5.

(*b*) Add chlorine water, a few drops at a time, to a mixture of a drop of a dilute potassium iodide solution with a few cubic centimeters of water and some chloroform. Shake the mixture after each addition of chlorine water and add the latter until the violet color of the iodine in the chloroform has disappeared. Read Smith or Remsen on iodine chloride and iodic acid.

4. (*a*) Add dilute sulphuric acid and a little sodium nitrite and starch solution to a mixture of potassium chloride, bromide and iodide (test for **iodides**).

---

[1] On account of the inflammability and the odor of carbon disulphide, chloroform is preferable for ordinary purposes. It has been observed in this laboratory, however, that the normal color of iodine in chloroform solution is sometimes not shown in the presence of certain organic substances, whereas the carbon disulphide test for iodine responded under the same conditions.

(*b*) Add chlorine water, in the same way as in 3 (*b*), to a mixture of a drop each of dilute potassium iodide, bromide and chloride solutions (diluted with 2 or 3 c.c. water) and 3 to 5 c.c. chloroform.[1] Add the chlorine water very gradually, shake the tube after every addition of it, and note whether a violet chloroform solution is obtained after the addition of the first chlorine water (test for **iodides**). Continue adding chlorine water in the same way, gradually, until the further addition *does not darken* the *supernatant aqueous layer* by the liberation of more iodine, but, if anything, makes it paler; then shake the mixture again vigorously and decant the supernatant aqueous layer from the chloroform solution of iodine, which latter is discarded. The aqueous solution contains all the bromide. Add one or two cubic centimeters of chloroform to it, and continue adding chlorine water slowly as above, until the violet color of the chloroform disappears, then observe whether a brown chloroform solution of bromine is formed by the careful addition of more chlorine. (Test for **bromides** in the presence of iodides and chlorides.)

(*c*) Treat a similar mixture of potassium iodide, bromide and chloride with an excess of minium (or, better, lead dioxide) and acetic acid. Boil the mixture until the vapor does not show the presence of free iodine or bromine, when tested with filter paper dipped into a starch solution containing potassium iodide;[2] then filter the solution and add silver nitrate and nitric acid to a small part of the filtrate. A pure *white* precipitate is silver chloride. (Test for **chlorides** in the presence of iodides and bromides.) If the color of the precipitate is not pure white, but even faintly yellow, the bromine or iodine has not been completely expelled. The treatment with acetic acid and minium or lead dioxide is continued and repeated until a pure white precipitate results.

5. Iodide, bromide and chloride ions may be detected in the presence of one another also by the following method,[3] based, like the one given in 4, on the fact that iodide-ion is most easily oxidized (to iodine), that bromide-ion is less readily oxidized (to bromine) and that chloride-ion resists oxidation most strongly (Chapter

---

[1] In the presence of organic matter, carbon disulphide is used in place of chloroform.

[2] A fairly sensitive test may be obtained with filter paper and potassium iodide solution (without starch).

[3] W. A. Noyes, *Qualitative Analysis* (1905), p. 74, recommends this method.

XIV). Prepare a mixture of a drop each of potassium iodide, bromide and chloride solutions, and dilute the mixture with 2 or 3 c.c. of water.

(*a*) Acidify the solution with 5 c.c. of sulphuric acid and add a few drops of ferric sulphate solution. Add a few particles of pumice stone to the mixture and boil the solution vigorously in a small flask or large test tube; test the vapor for **iodine** with starch paper. If iodine is found, boil the mixture until all the iodine is removed, adding a drop of the ferric sulphate solution, as needed, to insure the presence of an excess of the oxidizing agent.

(*b*) When the iodine is completely removed, add a few drops of potassium dichromate solution to the mixture, boil it again, and test the vapor for **bromine** with the aid of potassium iodide starch paper (prepared as in 4 (*c*)).

(*c*) If bromine is found, boil the liquid until the test paper shows that bromine has been completely expelled; add a drop or two of dichromate before the final test in order to insure the presence of an excess of the oxidizing agent. After all the bromine has been expelled, cool the solution, dilute it to about 10 c.c. and add silver nitrate to it; a white precipitate would prove the presence of **chloride-ion.**

Give the reaction equation for the oxidation of iodide-ion by ferric-ion in (*a*), and the equation for the oxidation of bromide-ion by dichromate in (*b*) (see Chapter XVI). Which must be the more powerful oxidizing agent?

Hydrocyanic Acid, HCN; *Cyanide-ion,* CN^-

NOTE. Particular care must be taken with this acid on account of its poisonous character. Its fumes should not be inhaled, a strong acid should not be used on its salts, and care should be taken not to cut the hands while the acid and its salts are used. Note the faint, but characteristic, odor of the acid by wafting the air above potassium cyanide towards you (*do not inhale it directly*).

1. Add potassium cyanide gradually to silver nitrate until no further change occurs. Recall § 3, p. 43, under silver and state why the precipitated silver cyanide redissolves in an excess of the reagent. Would the absence of a precipitate, on the addition of a few drops of silver nitrate solution to a salt solution, be any reliable evidence of the absence of cyanide?

2. Carry out the two following experiments side by side:

(*a*) To a few drops of potassium cyanide solution add a little ferrous sulphate, some ferric chloride and some sodium hydroxide. Warm the mixture and then add to it hydrochloric acid. (*Characteristic test for cyanide-ion.*) What is the precipitate? Add sodium hydroxide to it.

(*b*) Repeat every step of (*a*), but *leave out the cyanide entirely*.

For the identification of cyanide-ion by this method, the complex ferro- or ferricyanide-ion must be *prepared* in *alkaline* solution, and then *tested* for in *acid* solution.

3. To a drop of potassium cyanide solution add 2 c.c. of yellow ammonium sulphide, evaporate the mixture to dryness on the steam bath, and add ferric chloride and hydrochloric acid to the residue, dissolved in water (*characteristic test for cyanide-ion*).

4. (*a*) Try 1 and 2 (*a*) with a fresh solution of mercuric cyanide.

(*b*) Add sodium hydroxide to mercuric nitrate and then to the cyanide. What is peculiar in the behavior of this cyanide? To what are the peculiarities due? Recall the conductivity of mercuric cyanide solution (Chapter VI, p. 115).

(*c*) Add hydrogen sulphide and some hydrochloric acid to mercuric cyanide. What does this test show? How would you proceed to identify cyanogen in mercuric cyanide?

Sulphocyanic Acid, $HSCN$; *Ferrocyanic Acid*, $H_4[Fe(CN)_6]$; *Ferricyanic Acid*, $H_3[Fe(CN)_6]$

1. What metal ions are identified with the aid of the ions of these acids? How would you use the same reactions to identify:

(*a*) Sulphocyanide-ion?
(*b*) Ferrocyanide-ion?
(*c*) Ferricyanide-ion?

2. Add some silver nitrate to solutions of a salt of each acid.

V. PHOSPHATE GROUP

Hydrofluoric Acid, H_2F_2; *Fluoride-ion*, $F_2^{=}$

1. The addition of calcium chloride to a solution containing fluoride-ion (*e.g.* an ammonium fluoride solution) precipitates calcium fluoride, which is insoluble in water and in acetic acid but soluble in strong acids. Calcium oxalate is the only other calcium salt showing a similar behavior. When the insolubility of calcium

fluoride in acetic acid is used as a test for fluoride-ion, the presence of the latter must be confirmed by some other characteristic test (see 2 and 3), or the absence of oxalate-ion must be proved.

2. Cover one surface of a watch crystal with a film of paraffin, remove part of the paraffin from the glass, by writing with a sharp-pointed glass rod or pin on it, and expose the prepared surface to the fumes of hydrofluoric acid, obtained from a mixture of calcium fluoride and concentrated sulphuric acid in a lead dish (store-room). The dish should be placed in a warm, but not hot, place. In the presence of a fluoride the glass is etched (*test for a fluoride*).

3. Mix a little fluorspar with an equal bulk of silica in a very small test tube (2 to 3 c.c. capacity). Add two or three drops of concentrated sulphuric acid to the mixture, warm it gently and hold a film of water, in a loop of a platinum wire, over the opening of the test tube. A white deposit, silicic acid, should be formed on the water. This is the most convenient *test for a fluoride*. (See p. 70, under silicic acid, for the explanation of the reaction.)

Phosphoric Acid, H_3PO_4; *Phosphate-ion*, $PO_4^{\equiv}$

1. Test solutions of the following salts with neutral litmus paper: (*a*) NaH_2PO; (*b*) Na_2HPO_4; (*c*) Na_3PO_4. Add a few drops of methyl orange solution to: (*d*) H_3PO_4; (*e*) NaH_2PO_4. What conclusions may be drawn, from the different behavior of the solutions, as to the tendency of the hydrogen in phosphoric acid to form hydrogen-ion? (See Chapter VI, p. 102.)

2. With the exception of the alkali phosphates and acid phosphates, phosphates are insoluble in water. They are soluble, however, in acids. The most characteristic precipitates are $Mg(NH_4)PO_4, 6\,H_2O$ and Ag_3PO_4.

(*a*) Add a mixture of magnesium nitrate, ammonium nitrate and ammonium hydroxide ("magnesium nitrate mixture") to a solution of sodium phosphate. The crystalline precipitate, $Mg(NH_4)PO_4, 6\,H_2O$, is a *characteristic test for phosphate-ion* in the absence of arseniate-ion (see p. 54, § 3 (*b*)). It is formed only in neutral, or in alkaline (ammoniacal), solutions.

(*b*) Add a little silver nitrate to a solution of sodium phosphate. To a portion of the yellow precipitate, Ag_3PO_4, suspended in the liquid, add nitric acid; to the remainder add a solution of ammonia (see p. 42). Then carefully cover the nitric acid solution with a layer of dilute ammonia solution and observe the neutral zone at the junction of the two solutions.[1]

Although the tests 2 (*a*) and (*b*) are characteristic and are useful in certain cases, their application is limited by the fact that neither precipitate is formed in a strongly acid solution.

3. (*a*) Dissolve 0.1 gram of calcium phosphate in 2 c.c. of nitric acid and dilute the solution to 10 c.c. Add, first, a drop of the solution to 10 c.c. of "ammonium molybdate solution" (*nitric acid solution*[2]), and, after about a minute, add all of 1 c.c. and then 4 c.c. more of the solution to the mixture. The yellow precipitate is ammonium phosphomolybdate, $(NH_4)_3PO_4, 12\,MoO_3, 6\,H_2O$, and forms a *characteristic test for phosphate-ion* (Chapter XVI, p. 305). Conforming to its composition, the precipitate always requires a large excess of molybdate solution for its formation. Add to the remaining 5 c.c. of the nitric acid solution of calcium phosphate 1 c.c. of the molybdate solution and observe the result.

(*b*) Let the precipitate, obtained in (*a*), subside, decant the liquid, wash the precipitate twice, by decantation, with a little ammonium nitrate solution, dissolve it in a few drops of ammonium hydroxide solution and add some magnesium nitrate mixture to the solution. Collect the precipitated magnesium ammonium phosphate on a very small filter, wash it with some water, dissolve it in a little acetic acid, add silver nitrate to the solution, and, if yellow silver phosphate is not precipitated, cover the mixture with a layer of dilute ammonia. At the junction a zone of the yellow silver phosphate will appear (*characteristic tests for phosphate-ion*).

The molybdate test is the most valuable test for phosphates, because it can be carried out in acid (nitric) solution. Most phosphates that are insoluble in water dissolve in nitric acid. The subsequent tests with magnesium and silver salts are confirmative tests. Arsenic acid, H_3AsO_4, gives a similar arsenomolybdate (p. 54), which is formed only when the mixture is strongly heated (difference from *phosphate*). It yields a red silver arseniate. If arsenic is present, it is best removed, by precipitation with hydrogen sulphide, before the phosphate test is made.

---

[1] Silver arsenite shows a similar behavior and color.

[2] If a molybdate solution "without nitric acid" is used (see table of reagents), add 5 c.c. of dilute nitric acid and some ammonium nitrate to 5 c.c. of the molybdate solution, before making the test.

Boric Acids[1]

1. Prepare a rather concentrated solution of borax (sodium tetraborate $Na_2B_4O_7$) in water and add, to a part of it, some silver nitrate. The white precipitate is silver metaborate $AgBO_2$. Then dilute 1 or 2 c.c. of the borax solution with 50 c.c. of water and add silver nitrate to it. What is the brown precipitate and to what action of water on borates does it owe its formation? Why does water have this effect (Chapter X)?

2. Dip a piece of turmeric paper into a borate solution, dry the paper on a watch crystal over a steam bath, moisten it with dilute hydrochloric acid and dry it again. The red tint produced is a very characteristic *test for boric acid.*

3. Add, to a few drops of a borate solution in a porcelain dish, 10 c.c. of concentrated sulphuric acid and 10 to 20 c.c. of alcohol and light the alcohol. The green-edged flame, in the absence of copper, chlorides and bromides, is characteristic of *boric acid.*

In the presence of sulphuric acid, boric acid combines with alcohol to form a readily volatile ester, ethyl borate (see ethyl acetate under Acetic Acid, p. 82, and methyl salicylate under Salicylic Acid, p. 86). The action is: $3\ C_2H_5OH + H_3BO_3 \rightleftarrows (C_2H_5)_3\ BO_3 \uparrow + 3\ H_2O$. What effect must be produced on the reversible reaction by the affinity of concentrated sulphuric acid for water?

4. Mix a crystal of a borate with a little ammonium fluoride in a mortar (Care! Do not get the fluoride on the fingers!), or with a mixture of calcium fluoride and potassium acid sulphate, and heat a little of the mixture on the platinum wire in the edge of the bunsen flame. The spectrum of the boron flame (see *flame spectra,* p. 7) is very characteristic and may be used with advantage to identify boric acid with absolute certainty. The test may be made almost as sensitive as the spectrum analysis test for the alkalies.[2]

Oxalic Acid. (See below, p. 81, Group of Organic Acids.)

VI. NITRATE GROUP

Nitric Acid, HNO_3; *Nitrate-ion,* NO_3^-. (*Nitrous Acid,* HNO_2; *Nitrite-ion,* NO_2^-)

1. Heat in a narrow glass tube, sealed at one end, some lead nitrate; some potassium nitrate. If gases are evolved, identify them.

---

[1] Read Smith or Remsen on the various boric acids.

[2] See Vogel's *Spectralanalyse,* pp. 294–295, and Landauer-Tingle's *Spectrum Analysis,* p. 102.

2. Add a drop of sodium nitrate solution to a mixture of 2 c.c. of water and 2 c.c. of concentrated sulphuric acid, cool the mixture and cover it carefully with a layer of 5 c.c. of ferrous sulphate solution. Observe the zone of contact against white paper. The brown substance formed is probably $FeSO_4,NO$. (*Characteristic test for nitrate-ion,* but see § 4.)

3. Add some zinc and iron dust to a drop of sodium nitrate solution mixed with a few cubic centimeters of sodium hydroxide solution. Heat the mixture and test the vapor with litmus paper for ammonia. How could this test be used in the presence of an ammonium salt? Explain the reaction.

4. (*a*) Use a drop of potassium *nitrite* solution for the test given in 2. Would it also give the reaction in 3?

(*b*) Add dilute sulphuric acid to a potassium nitrite solution. Then add a drop of potassium iodide and chloroform or some starch solution to the mixture. (Differences from *nitrates.*)

(*c*) Nitrite-ion may be destroyed as follows: Dilute 1 c.c. of potassium nitrite solution with 10 c.c. of water, add a gram of ammonium sulphate to the solution and boil the mixture for 15 to 30 minutes in a test tube clamped in a slanting position. A drop of the solution is then tested as in (*b*). If nitrite is still indicated, the treatment must be continued to destroy it completely according to the action[1]: $NH_4NO_2 \rightarrow N_2 + 2\,H_2O$.

(*d*) Add 0.1 c.c. of a 0.001 molar solution of potassium nitrite to 10 c.c. of water; add 2 or 3 c.c. of sulphanilic acid-naphthylamine solution to the liquid and warm the mixture: the pink color produced (an aniline dye) is a sensitive and *specific test for nitrites.*

Chloric Acid, $HClO_3$; *Chlorate-ion,* ClO_3^-

1. (*a*) Add silver nitrate to a potassium chlorate solution.

(*b*) Heat some dry potassium chlorate in a narrow glass tube; test the gas evolved. Dissolve the residue in water and add silver nitrate and some nitric acid to this solution.

2. Drop a *little* potassium chlorate on a piece of charcoal heated to redness before the blowpipe.

3. Add a *very little* potassium chlorate (a few crystals) to a drop or two of concentrated sulphuric acid in a porcelain dish. (Care! the gas evolved is explosive!) Note the color and odor of

---

[1] Preparation of nitrogen. See also Böttger's *Qualitative Analyse,* p. 311.

the gas and its action on litmus paper. (Larger quantities of chlorate can produce very dangerous explosions with concentrated sulphuric acid!)

VII. The Group of Organic Acids

1. Mix a salt of any organic acid with an equal amount of cupric oxide powder, put a little of the mixture into the sealed end of a narrow glass tube four inches long, heat the open end of the tube and draw it out to a rather wide and long capillary, bent at a right angle to the tube. Cut off all but two or three inches of the capillary. Then heat the copper oxide mixture *slowly* and pass any evolved gases into limewater, using the capillary as the delivery tube. Calcium carbonate is precipitated.

All *organic* compounds (as well as most carbonates) give this test. If the cupric oxide is not known to be free from organic matter, its purity should be ascertained by a blank test.

If a *carbonate is present* and it is desired to apply this test, in order to ascertain the presence or absence of other organic matter, proceed as follows: in the case of a solid substance, decompose the carbonate by adding dilute hydrochloric or sulphuric acid, drop by drop, to the substance. As soon as the evolution of carbon dioxide ceases, warm the mixture gently for a moment, then cool it, neutralize it with a clear solution of barium hydroxide and evaporate the water. The residue, dried at 100°, is tested as described above. If a solution is under examination, it is rendered slightly alkaline with barium hydroxide solution (any precipitate, that may form, is allowed to remain in the mixture) and the mixture evaporated to dryness. The residue is treated with acid, etc., as just described for a solid substance.

The treatment with acid will allow hydrocyanic acid to escape, but it would be readily recognized by its faint but characteristic odor (Care!). Inert, volatile organic compounds, such as alcohol, would escape when a solution is evaporated, and volatile organic bases would escape from an alkaline solution. In a comprehensive analysis for organic compounds, the solution would be subjected to distillation and the distillate examined for such volatile compounds. The process, described above, will suffice for the recognition of the presence of the organic acids included in this book, as well as of such organic matter (gelatine, etc., see Chap. VII) as might interfere with the systematic method of elementary analysis used.

2. Heat some potassium oxalate and some sodium potassium tartrate on porcelain crucible lids and note the difference in their behavior.

Acetic Acid, CH_3COOH; *Acetate-ion,* $CH_3CO_2^-$

1. Add some concentrated sulphuric acid to a little solid sodium acetate, warm the mixture and note the odor of the liberated acetic acid.

2. Mix equal volumes (3 or 4 c.c.) of concentrated sulphuric acid and alcohol, adding the acid slowly to the alcohol and cooling the mixture under the tap (Care!). Add to the mixture some solid sodium acetate and heat the solution for 5 or 10 minutes in a water-bath, the test tube being closed with a loose plug of cotton. Compare the odor of the ethyl acetate, that is formed (*test for acetic acid*), with the odor of a fresh mixture of alcohol and acetic acid. The ester is formed according to:[1] $CH_3COOH + C_2H_5OH \rightleftarrows CH_3CO_2C_2H_5 + H_2O$.

3. Heat a small crystal of sodium acetate in a glass tube with a minute quantity of arsenic trioxide. Cacodyloxide, $[(CH_3)_2As]_2O$, is formed and recognized by its odor (Poison!).

Other organic acids of the acetic acid series, *e.g.* propionic acid, give a similar test.

Oxalic Acid, $H_2C_2O_4$; *Oxalate-ion,* $C_2O_4^=$

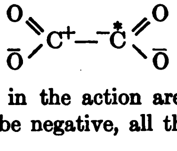
1. Add some calcium chloride to ammonium oxalate, then acidify the mixture with acetic acid. Calcium oxalate and calcium fluoride (*q. v.*) are the only common calcium salts insoluble in acetic acid.

2. Treat a mixture of ammonium oxalate and dilute sulphuric acid, in the cold, with some finely powdered manganese dioxide. What gas is evolved? This is a most convenient *test for an oxalate.*

The oxidation may be expressed by the equation:

$$H_2C_2O_4 + MnO_2 + H_2SO_4 \rightarrow 2\,CO_2 + MnSO_4 + 2\,H_2O.$$

According to the electric theory of oxidation and reduction, the ion Mn^{++++} may be considered to be the oxidizing agent, giving up two positive charges and going over into manganous-ion Mn^{++}. Oxalate-ion $C_2O_4^=$ may be considered to be:

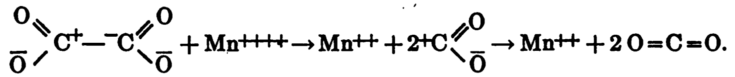


Only the charges involved in the action are indicated. All the oxygen valences may be assumed to be negative, all the remaining carbon valences

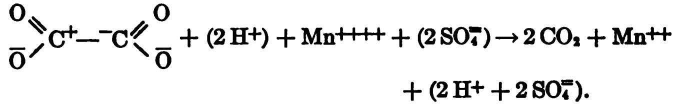
---

[1] $C_2H_5HSO_4$, ethyl acid sulphate, is an intermediate product.

positive. In carbon dioxide all the carbon valences must be considered positive. The oxidation consists, then, in the transfer of the two positive charges to the carbon atom marked with*, one charge neutralizing the negative charge on it, and the other charging it positively;[1] the two carbon atoms, charged with the same kind of electricity, separate and carbon dioxide is formed:



Two hydrogen ions are liberated when an oxalate ion is converted into (electrically neutral) carbon dioxide, but a sulphate ion is simultaneously liberated by the reduction of Mn++++ to Mn++. The total action is:



The bracketed products do not enter directly into the action.

Tartaric Acid, $C_4H_6O_6$; *Tartrate-ion*, $(CHOH)_2(CO_2)_2^=$

1. Heat some sodium-potassium tartrate (Rochelle salt) on the lid of a porcelain crucible. Note the odor of the vapors.

2. (*a*) Add a little sodium hydroxide to copper sulphate and to aluminium sulphate solutions, separately.

(*b*) Repeat (*a*), but, before the addition of the alkali, add an excess of a concentrated solution of Rochelle salt to the copper and aluminium sulphates. (Recall the lecture experiments on complex metal ions formed with tartrates, Chapter XII, p. 240.)

(*c*) To determine whether the metal ions are completely suppressed (*cf.* the stability constant of complex ions), add ammonium sulphide to the mixture of copper sulphate and Rochelle salt and note whether the extremely insoluble copper sulphide can be precipitated.

3. (*a*) Add 5 c.c. of calcium chloride solution (an excess is required) and a few drops of ammonium hydroxide and ammonium chloride solutions to 2 or 3 c.c. of Rochelle salt solution. If a precipitate of calcium tartrate $CaC_4H_4O_6, 4H_2O$ does not form in a few moments, shake the liquid vigorously and rub the walls of the test tube with a glass rod, in an effort to start crystallization. Collect the precipitate on a filter and wash it well with water.

(*b*) Put a stick (two inches) of solid sodium hydroxide into a test tube, cover it with water and, after a few moments, pour away the solution of the outside crust, which usually contains considerable carbonate. Dissolve the rest of the sodium hydroxide in a little water. Then treat the larger part of the calcium tartrate obtained in (*a*) with this sodium hydroxide solution. It will dissolve as the sodium salt of the complex calcium-tartaric-acid, $Na_2(C_4H_2(O_2Ca)O_4)$. Dilute the solution, filter and boil it. Calcium tartrate is reprecipitated (*characteristic test*).

---

[1] See Chapter XV, p. 293, on the production of an electric current by the oxidation of formaldehyde.

(*c*) To a very small portion of the calcium tartrate, obtained in (*a*), add four or five drops of silver nitrate and a few drops of ammonia solution. Boil the mixture vigorously in a test tube, allowing it to evaporate nearly, but not quite, to dryness. A silver mirror is formed.

Benzoic Acid, C_6H_5COOH; *Benzoate-ion*, $C_6H_5CO_2^-$

1. (*a*) Add to a (rather concentrated) solution of sodium benzoate an excess of hydrochloric acid; collect the precipitated benzoic acid on a very small filter and wash it with a little water as thoroughly as possible; use the filter pump to drain the precipitate well. Then press the precipitate on a small piece of clean clay plate and let it dry. Place a little of the dried substance in a melting-point tube,[1] shaking the material down to the bottom of the tube. Mix another small portion of it with about an equal quantity of pure benzoic acid and put the mixture into a second melting-point tube. Then determine the melting point[2] of the

---

[1] A clean glass test tube or a piece of wide glass tubing is heated in a blast-lamp flame along a space about one inch wide, until the glass softens; it is withdrawn from the flame and drawn out to a long capillary tube of 1 to 1.5 mm. internal diameter (see specimen tubes). Seal off, at both ends, lengths of the capillary of about 10 cm. When a melting point is to be determined, the capillary tube is cut in two, the tube having thus been kept clean and dry.

[2] Fasten a thermometer in a cork and clamp it, by means of the cork, so that its bulb is immersed in glycerine in a beaker (50 c.c.), which is a little more than half full. The beaker should be placed on iron wire gauze whose edges are turned down over an iron ring of a ring stand in such a way, that the beaker is not likely to be upset. A stirring rod, bent so as to form, at one end, a ring that can be slipped around the bulb of the thermometer, and so as to have a handle at the other end, is used to stir the bath during the determination of a melting point. A melting point tube is placed against the sides of a thermometer in such a way, that the substance in the tube is near

mixture and of the precipitate. As benzoic acid melts at 121°, the bath may be heated rather rapidly to 100–105°, but then it is heated very slowly to 121° and stirred continually, the contents of the melting-point tubes being carefully observed. If the precipitated acid and the mixture melt at the same point, the *identity of the former may be considered established.* If the precipitated acid melts, say, at 119° (the melting point being depressed by the presence of a trace of impurity) and *the mixture melts higher* (between 119° and 121°), the identity of the acid is practically certain.[1] In such a case it would be well, in important work, to sublime the precipitated acid carefully, in a dry test tube or between two watch glasses, and to repeat the test with the sublimed acid.

(*b*) Mix a little benzoic acid with about the same quantity of salicylic acid (melting point 155°) and determine the melting point of the mixture.

2. Add a dilute solution of ferric chloride to a solution of sodium benzoate: the flesh color of the precipitate is characteristic.

3. Add 2 c.c. of concentrated sulphuric acid slowly (Care!) to 2 c.c. of methyl alcohol, cooling the mixture during the process. Add a little benzoic acid or sodium benzoate to the mixture and warm it for ten to fifteen minutes in a steam bath. The test tube may be lightly closed[2] with some cotton during the heating process; then remove the cotton and note the characteristic odor

---

the middle of the mercury bulb and the open end of the tube well above the liquid. The surface tension of the liquid will hold the tube against the thermometer.

[1] Except in exceedingly rare and well-defined cases (see Walker's *Introduction to Physical Chemistry* (1909), p. 71; see also p. 74) the melting point of a substance is *depressed* by the admixture of any impurity or foreign substance, that is soluble in the compound. If a substance is simply found to melt at 121° (the melting point of benzoic acid), its identity with benzoic acid would not be established; it might be quite a different substance. But in the latter event, when benzoic acid is added to it, provided the mixture is found to melt to a clear liquid, the melting point of the mixture would be found much lower than that of the original substance — it might be depressed as much as 10 to 20 degrees, although each substance alone melts at 121°. In such a case, too, the mixture would not show a sharp melting point, but would soften and fuse through a range of several degrees. For these reasons, the determination of the melting point of a mixture of the substance to be identified with a known pure sample of the substance it is suspected to be, is one of the most simple and direct methods of proving or disproving identity.

[2] Böttger's *Qualitative Analyse* (1908), p. 315.

of the methyl benzoate $C_6H_5CO_2CH_3$, which has been formed. In identifying benzoic acid by this process, the odor, obtained from an unknown substance under examination, is compared with the odor obtained from known benzoic acid.

Salicylic Acid, $C_6H_4(OH)COOH$; *Salicylate-ion,* $C_6H_4(OH)CO_2^-$

1. Determine the melting point of the acid.
2. Add a dilute solution of ferric chloride to a dilute aqueous solution of some of the acid.
3. Treat a little salicylic acid with methyl alcohol and sulphuric acid, as described under benzoic acid in § 3. Methyl salicylate (oil of wintergreen) is formed and may be identified by its odor.

PART IV

SYSTEMATIC ANALYSIS

A. PRELIMINARY EXAMINATION

THE unknown, if it is a solid other than a metal or an alloy, should be reduced to a coarse powder; it is advisable to pulverize a very small trial portion first, as a safeguard against mixtures which may explode as the result of friction or concussion.

1. Before the systematic wet analysis is undertaken, the substance may be subjected to a few short preliminary tests, which may throw considerable light on its nature and may facilitate the rigorous analysis. Particular attention should be paid to the following results of the preliminary tests, as they modify the course of the subsequent systematic analysis. For the same reason, the tests involved, at least, should never be omitted, unless the appearance of the substance makes them clearly unnecessary.

(1) **Carbonization** in the *dry heat test*, **2,** with the emission of the odor of burnt organic matter, or carbonization by sulphuric acid (see 1 (*a*), 1 (*b*) under **7**), indicates the presence of organic substances,[1] which, without due precautions, *may interfere with the detection of some of the metals of the aluminium, alkaline earth and*

---

[1] The only organic substances considered in this course are the organic acids described in Part III. Many other organic substances, such as gelatine, albumins etc., interfere not only with the detection of the metals of the aluminium, alkaline earth and alkali groups, but are also liable to interfere with the precipitation of the silver, copper and arsenic groups (as well as of those just mentioned), by producing *colloidal suspensions* (see Chapter VII). The occurrence of such a condition is usually indicated by the formation of *opalescent* mixtures (for instance, when hydrochloric acid is added for the precipitation of the silver group, or hydrogen sulphide for the precipitation of the copper and arsenic groups). In the presence of very small quantities of a precipitate even this indication may be absent. For a proper analysis of such mixtures the organic matter should be completely destroyed by one of the methods described by Fresenius, pp. 570 to 581. As a rule, fusion with sodium carbonate and nitrate (as below, p. 108) or treatment with conc. sulphuric acid (as below, p. 115) is the simplest and most effective treatment.

alkali groups (see p. 107). The precautions given in the systematic part are then observed (pp. 108, 115, etc.).

(2) If the metaphosphate bead and the fluoride tests **5** (1) show that a **silicate** is present in quantity, the special method of analysis for *silicates* should be followed (pp. 135–6).

(3) If **cyanogen** compounds are clearly indicated by the preliminary tests **2** (1) and **7** (1), and if the compounds are insoluble, students should use the special method for the analysis of cyanogen derivatives, Fresenius, p. 529. The comparative stability of the complex cyanide ions renders this course necessary.

(4) If **fluorides** are found in **7** (1), all operations with acid solutions, except brief tests, are carried out, as far as possible, in platinum vessels.

A record should be kept of each analysis according to the following illustration. The observations and conclusions should be recorded while the analysis is being made, not after its completion.

ILLUSTRATION.[1]

No.	Substance.	Reagent.	Observations.	Conclusion.
1	Unknown 1	Dry heat	Undecided	
2	Do	Blowpipe	Brown incrustation	Cd
3	Do	Metaph. bead.	Undecided	
4	Do	H_2O	Neutral solution	
5	Solution 4	HCl	No precipitate	Absence of Ag, etc.
6	Do 5	H_2S	Yellow precipitate	Cd, As, Sn.
7	Precipitate 6	$(NH_4)_2S$	Insoluble	Cd

The numbers 4, 5, and 6 refer to the solution (precipitate, filtrate) *obtained* in *line* 4, 5, etc.

I. *The Examination of a Non-metallic Solid*

2. Heat a little of the solid substance in the sealed end of a narrow glass tube three inches long. Note all changes, as indicated in the following subheads. *Care* must be taken in observing the odors of gases formed (*HCN is poisonous*): only a very little of the gas is inhaled if the tube is moved to and fro before the nose, while *short* breaths are taken to obtain trial whiffs. If in doubt as to the interpretation of the result, proceed with the analysis — the tests are largely *indications*, and the wet analysis will ultimately remove the doubt.

---

[1] The forms of this table and of those that follow are analogous to those used by W. A. Noyes, *loc. cit.*

Observation and Test.	Conclusion.
(1) A gas is formed.	
(a) Brown, odor of NO_2	Nitrates.
(b) Brown, odor of Br	Bromides.
(c) Violet	Iodides.
(d) Yellow, odor of chlorine	Chlorides.
(e) Inflammable, blue flame	CO, oxalates, etc.
(f) Inflammable, crimson flame	*Cyanogen* from *cyanides*.
(g) Odor of SO_2	Sulphur derivatives.
(h) Odor of HCN[1]	Cyanides.
(i) Odor of H_2S	Sulphides, etc.
(j) Odor of ammonia. Litmus.	Ammonium salts, *cyanides*.
(k) Glowing splinter ignites	Oxygen, from the oxide of a noble metal, a higher oxide, a peroxide,[2] chlorate, nitrate.
(l) Drop of lime water, cloud.	Carbonates, *organic compounds*.
(m) Steam. Colorless liquid condenses.	Water, mechanical, crystallization, or constitutional.
(2) A sublimate is formed.	
(a) White. Lime test, NH_3	Ammonium salts.
(b) White, sublimes without fusing, yellow, while hot.	HgCl.
(c) White, fuses	$HgCl_2$.
(d) White, fuses to a yellow liquid.	Sb_2O_3.
(e) White, brilliant crystals	As_2O_3.
(f) White, combustible vapors.	Organic acids.
(g) Metallic globules	Hg, from oxide, etc.
(h) Yellow or yellowish brown, inflammable with SO_2 odor	S.
(i) Yellow	As_2S_3.
(j) Yellow, red by rubbing	HgI_2.
(k) Black, violet vapor	I.
(l) Black, colorless vapor	As (mirror-like).
(m) Black, red by rubbing	HgS.

---

[1] A more satisfactory and more sensitive test for hydrocyanic acid is made as follows: bring a film of NaOH solution into the loop of a platinum wire, hold the film for a minute, in the vapor that is to be tested, transfer the droplet to a white porcelain surface, add, with a pointed glass rod, a minute drop of a fresh solution of ferrous sulphate and then, after a few moments, a drop of hydrochloric acid to the test: a blue (Prussian blue) or deep green tint shows the presence of hydrocyanic acid in the vapor tested. The ferrous sulphate is oxidised sufficiently, during the making of the test, to supply the mixture of ferri- and ferro-ion required (p. 76).

[2] $Ba(O_2)$ is a *peroxide*, a salt of hydrogen peroxide; MnO_2 and PbO_2 are *dioxides*.

Observation and Test.	Conclusion.
(3) The substance changes color and turns:	
(a) Black, odor of burnt organic matter, organic gases, H_2O.	**Organic substances.**
(b) Black, without signs of organic matter.	Black metal oxide, *e.g.* of Cu, Ni, Co, Mn, etc.
(c) Yellow; cooled, white	ZnO.
(d) Yellowish brown; cooled, light yellow.	SnO_2.
(e) Brown-red. Fuses easily. Cooled, yellow.	PbO.
(f) Orange. Fuses, but with difficulty. Cooled, pale yellow.	Bi_2O_3.
(g) Dark brown, hot and cooled.	Mn_3O_4.
(h) Dark brown; cooled, reddish.	CdO.
(i) Dark red to black; cooled, red.	F_2O_3.

3. Treat a mixture of the substance and sodium carbonate with the **blowpipe flame.** The effect of the ***reducing flame*** is given, unless the oxidizing flame is specified. Note any metal bead that may form in the cavity, as well as any incrustation around the cavity. Metallic globules should be examined in regard to brittleness, malleability and color. If no larger globules are seen, the contents of the cavity are crushed in a mortar, carbon and soluble matter washed away by decantation, and any residue vigorously rubbed: mortar and pestle are then examined for glittering particles.

Observation and Test.	Conclusion.
(1) Metallic particles without incrustation.	
(a) Color: yellow, white, red	Au, Ag, Cu.
(2) *Malleable* beads with incrustation.	
(a) Faint yellow incrustation, hot; cold, white.	Sn.
(b) Yellow incrustation, hot and cold	Pb.
(3) *Brittle* beads with incrustation.	
(a) Yellow incrustation, hot and cold	Bi.
(b) White incrustation, white fumes	Sb.
(4) Magnetic particles	Fe, Ni, Co.
(5) Garlic-like odor	As.
(6) Reddish incrustation, no bead	Cd.

4. Heat the substance on charcoal before the **blowpipe flame** without the addition of sodium carbonate.

Observation and Test.	Conclusion.
(1) The mass fuses, is absorbed by the charcoal.	Alkali metal salts.
An infusible white mass is formed.	
(a) Litmus, alkaline....................	Alkaline earths.
(b) Heated with $Co(NO_3)_2$, blue..........	Alumina (silica, phosphates).
(c) Heated with $Co(NO_3)_2$, green.........	Zinc salt.
(d) Heated with $Co(NO_3)_2$, violet........	Magnesium salt.
(3) Lively combustion of charcoal..............	Chlorates, nitrates.
(4) Incrustations, etc., as in **2** (2) and (3).	

5. Heat a coarse grain or two of the substance in the **metaphosphate bead** in the oxidizing flame of the Bunsen burner.

Observation.	Conclusion.
(1) "Skeleton" in the bead.	
(a) Colorless "skeleton". [*Test the original substance for* SiO_2 *by* SiF_4 *test* (§ 4, p. 70).]	Silicic acid; stannic acid.
(b) Metallic particles....................	Gold or platinum.
(2) The bead is colored, when hot (h) or cold (c).	
(a) Blue (h), blue (c)....................	Cobalt.
(b) Green (h), blue (c)..................	Copper.
(c) Green (h), green (c)..................	Chromium.
(d) Brown-red (h), light yellow to colorless (c); red (reducing flame) (h), greenish (c).	Iron.
(e) Reddish brown (h), yellow or colorless (c).	Nickel.[1]
(f) Yellowish brown (h), light yellow or colorless (c).	Bismuth.
(g) Violet (h), amethyst (c)..............	Manganese.

---

[1] A borax bead gives a better test for nickel: brown (c).

6. Moisten the substance with hydrochloric acid and test its behavior on a platinum wire in the **flame**. In case of doubt, match the flame color with that produced by a known sample of the substance suggested, held on a second wire next to that with the unknown.

Observation.	Conclusion.
(1) Intense yellow, persisting	Na.
(2) Violet to bluish	K, As, Pb, Sb.
(3) Crimson	Sr (Li).
(4) Brick-red	Ca.
(5) Green	Ba, Mn, H_3BO_3.
(6) Intense blue-green	Cu.

7. Warm some of the substance with **concentrated sulphuric acid** in a two-inch test tube. *Very little* should be tried first, as chlorates produce explosions. See the *precautions* given in **2** concerning the identification of odors.

Observation and Test.	Conclusion.
(1) Colorless gas:	
(a) Drop of limewater, cloud	CO_2, carbonates, organic acids.
(b) Acid blackened	**Organic** *matter*.
(c) Inflammable, blue flame	CO, oxalates, (formates), cyanides.
(d) HCN odor[1]	**Cyanides.**
(e) H_2S odor	Sulphides.
(f) SO_2 odor	Sulphites, or reducing agent.
(g) Fumes with NH_3; cloud with drop silver nitrate solution.	Chlorides.[2]
(h) Etches glass	**Fluorides.**
(2) Brown gas:	
(a) Br odor	Bromides.
(b) NO_2 odor	Nitrates, nitrites.
(3) Violet gas:	
Black sublimate	Iodides.
(4) Yellow gas:	
(a) Non-explosive	Chlorine, from hypochlorites.
(b) Explosive	Chlorates.

---

[1] See the test described in the footnote to **2** (1).

[2] $HgCl_2$, HgCl, AgCl, $PbCl_2$, do not evolve HCl readily.

II. *The Examination of a Metallic Solid*

8. 1. The **blowpipe** test, without sodium carbonate, in the reducing flame is tried, as described above in **4.** Consult also **3.**

2. The substance is heated in a glass tube sealed at one end; a sublimate of Hg, As or Cd may be obtained.

9. A small portion is warmed with water acidified with acetic acid. An evolution of hydrogen indicates the presence of a light metal (alkali or alkaline earth metal, or manganese).

III. *The Examination of a Liquid*

10. Evaporate a portion of the liquid to see if a solid residue is left. Such a residue may be tested according to **2–7**; see particularly **1,** p. 87. If no residue is left, only volatile substances (ammonia, volatile acids, ammonium carbonate, arsenic chloride, mercuric chloride, hydrogen peroxide, volatile organic substances, etc.) can be present in the solution.

11. Test the solution with litmus paper.

1. If its reaction is *neutral,* the solution is ready for analysis for metal ions according to part **C** (p. 100), and for acid ions according to part **D,** p. 115.

2. If the solution has an *acid* reaction, a free acid is present or a hydrolyzed salt of a weak base and a stronger acid. The solution is also ready for analysis according to part **C,** p. 100, for metal ions, and according to part **D,** p. 115, for the acid ions.

3. If the solution has an *alkaline* reaction, a free alkali or alkaline earth is present or the hydrolyzed salt of one of these bases with some weak acid. Hydrochloric acid is added in moderate excess to the solution and the mixture is warmed.[1]

(*a*) *No precipitate is formed.* The acidified solution is ready for analysis according to part **C, 21,** p. 100, for the metal ions.

(*b*) *A precipitate is formed and redissolved in the excess of acid* (recall the behavior of aluminates, stannates and salts of similar amphoteric acids); the acid solution is analyzed according to part **C, 21,** p. 100, for metal ions. The evolution of hydrogen sulphide indicates the presence of a sulpho-acid salt (*e.g.* sulpharsenite, etc.); the evolution of hydrocyanic acid indicates the presence of complex cyanide salts. The odor of ammonia in the original solution (in the absence of hydrogen sulphide) indicates the presence of complex ammonium ions.

(*c*) *A precipitate is formed and not redissolved.* The acid solution is filtered and analyzed according to part **C, 21,** p. 100, for metal ions. *The precipitate is treated as a new unknown* and brought into solution according to part **B,** below, or, if it cannot be dissolved, it is analyzed as an " Insoluble Substance " for metal and acid ions, according to part **E,** p. 130. (See the previous paragraph (*b*) in regard to the significance of any evolution of a gas.)[1]

---

[1] See part **D,** p. 115, in regard to the treatment for the analysis for acid ions.

B. THE SOLUTION OF SUBSTANCES FOR THE SYSTEMATIC ANALYSIS FOR METAL IONS

I. *The Solution of a Non-metallic Solid*

12. The Selection of a Solvent. — Try to dissolve a little of the substance by using the solvents in the order: water, dilute hydrochloric acid,[2] concentrated hydrochloric acid, dilute nitric acid,[2] concentrated nitric acid, aqua regia (3 volumes of concentrated hydrochloric acid and 1 volume of concentrated nitric acid). A *small amount* of material (0.05 to 0.2 gram)[3] is tested with 1 to 10 c.c. (10 c.c. only in the case of *water*) of the solvents in the order given. If cold water or acid does not dissolve the substance, try the effect of heat before proceeding to the next solvent. If a substance dissolves with difficulty in an agent, its behavior towards the subsequent ones is ascertained before the solvent is definitely selected. If the substance is altogether or partly insoluble in water and the acids named, the insoluble part is analyzed according to special methods for "Insoluble Substances" (part **E,** p. 130). The presence of a (water or acid) soluble substance, besides an insoluble component, is recognized by the method described, for water, in the next paragraph.

It is, usually, advisable to ascertain whether a substance is *partially soluble in water*; if an insoluble residue is left in the treatment with hot water, decant the liquid through a small filter and evaporate a portion (about 1 c.c.) of the filtrate to dryness in a porcelain dish or on a watch glass. If more than traces of solid remain, the substance is partially soluble. The sample (0.05 to 0.2 gram) is then treated with more water (10 to 20 c.c.), to determine whether it cannot be completely dissolved. The *undissolved portion* is then treated with the acids in the order named.

---

[1] If hydrocyanic acid is evolved and a precipitate is formed, the substance should be examined according to Fresenius, p. 529.

[2] The dilute acids are hexamolar HCl and HNO_3. Whenever the use of these acids, as dilute acids or as acids *without any qualification*, is called for, the hexamolar acids are the ones intended to be used. *Concentrated acids are to be used only when instructions call for them specifically.*

[3] If only a little material is available for analysis (less than 3 to 5 grams) proportionally smaller quantities must be used throughout the course of analysis and the material must be carefully saved. With some experience, the selection of the solvent can be made by testing a few grains of material with a drop or two of the solvents.

In the *treatment with acid,* not more than 1 to 4 c.c. of an acid need be used for 0.05 to 0.2 gram material. Frequently it will be found that treatment with a small amount of acid (dilute or concentrated), followed by treatment with *water,*[1] is effective; hence, if an acid leaves a residue, the liquid is decanted and the solubility of the residue in water is ascertained before deciding whether the substance is completely soluble in the acid or not.

Frequently *all but a very slight portion of a substance is found to be soluble* in a given solvent. If the solvent is water, it is possible that a salt, soluble in water, has been partially hydrolyzed and a basic salt has been deposited. It is well then, before proceeding with the analysis, to ascertain if the slight residue cannot be dissolved in a drop or two of acid (hydrochloric or nitric) and to add the solution, if the residue dissolves, to the main aqueous solution. If a very slight residue is left, that is insoluble in acids, and its appearance indicates quartz or a silicate (*gangue in a mineral*), it is usually sufficient to confirm the presence of silicic acid with the aid of the metaphosphate bead test (p. 69).

Aqua regia, besides leaving undissolved components originally present, may lead to the separation of new insoluble substances, such as *sulphur* (yellow, light, may float), *silver chloride* (white, tends to form compact masses of adhering particles), *lead chloride* (white needles separate out, particularly when the liquid is cooled), *sulphates,* etc. If the substance is obviously attacked by aqua regia, the solvent should be used (but only when all the others have failed); any insoluble residue is analyzed according to part **E,** p. 130, and the rôle of the aqua regia in producing such insoluble compounds is taken into account.

All changes observed in the course of effecting solution, such as the *liberation of a gas* (CO_2, H_2S, HCN, NO_2, etc.), the *separation of a precipitate* (sulphur, silicic acid (*see* **1** (2), p. 88), etc.), a marked *change of color* (reduction of chromates, permanganates, oxidation of iodides, etc.), *must be carefully recorded and considered.*

---

[1] Certain salts, such as $BaCl_2$ or $Ba(NO_3)_2$, which are difficultly soluble in strong acids and easily soluble in water (p. 72), may be formed.

Having determined the best solvent for a substance, proceed, according to the results obtained, *to* **13–18,** *to prepare a solution for analysis.*

13. The Substance is Completely Soluble in Water. — 1. Dissolve a gram of the material in 30 to 60 c.c. of water; apply heat to facilitate the solution, but cool the liquid afterwards. As much as 100 to 150 c.c. of water may be used, *if necessary,* but if more than that volume is required, it is better to find the proper acid solvent.

2. *Test the reaction of the solution with litmus;* if it is *neutral* or *acid,* the solution is ready for analysis according to part **C,** p. 100; if it is *alkaline,* follow the instructions given in **11,** 3, p. 93.

14. The Substance is only Partially Soluble in Water. — Treat a gram of substance with 20 to 50 c.c. of hot water. The solution is treated according to **13,** 2, the undissolved residue **R** according to **15, 16, 17** or **18,** according to the indications obtained in **12** in ascertaining the selection of a solvent.

Ordinarily it is advisable to mix the aqueous solution, obtained, with an acid solution of the remainder of the material, as prepared in **15** to **17,** and to make an analysis of only one (the mixed) solution. But such a step must be expressly stated in a report. For certain purposes, such as soil, fertilizer and some mineral analyses, separate analyses of water-soluble, acid-soluble and acid-insoluble components are required.

15. Solution in Hydrochloric Acid. — If the preliminary trials, made according to **12,** have led to the selection of hydrochloric acid as the proper solvent for the substance, or for that part of it which is insoluble in water, a gram of the material, or the residue **R** left when a gram of the substance has been extracted with water (**14**), is dissolved in as little as possible dilute or concentrated acid or both. If possible, do not use more than 5 to 8 c.c. dilute acid or 3 to 4 c.c. concentrated acid. The solution obtained is diluted to 50 to 75 c.c. If a precipitate is formed by this dilution, it may contain $PbCl_2$, HgCl, or AgCl, especially if concentrated HCl was used, or it may consist of (BiO)Cl or (SbO)Cl. The first chlorides mentioned are somewhat more soluble in excess of concentrated acid, as complex acids (*e.g.* $HAgCl_2$), than in dilute acid, the complexes being decomposed when the solution is diluted. If the precipitate consists of (SbO)Cl or (BiO)Cl, it will redissolve readily when 1 or 2 c.c. of dilute acid are added to the mixture, while the first group of chlorides will remain precipitated. If a precipitate remains as the result of the dilution, and after the addition of 2 c.c. of dilute acid, it may be collected and analyzed according to **20,** p. 100; but it is best to try dilute nitric acid as a solvent of the original substance; in such a case it should usually prove much better than hydrochloric acid.

The hydrochloric acid solution is analyzed according to **C, 21,** p. 100. If more than the recommended amount of acid has been used, there may be too great an excess of acid present to make complete precipitation of the copper and arsenic groups with H_2S directly possible, but provision is made for the removal of the excess only after a first treatment with hydrogen sulphide. $HgCl_2$ and especially $AsCl_3$ are volatile, and the excess of acid is to be removed only after their sulphides have been precipitated.

16. Solution in Nitric Acid. — If the preliminary tests, made according to **12,** led to the selection of HNO_3 as the proper solvent for the substance, or for that part of it which is insoluble in water, a gram of the substance, or the residue **R** left when a gram of material has been extracted with water (**14**), is dissolved in as little as possible dilute or concentrated nitric acid, or both. Use 5 to 8 c.c. of the dilute, or 3 to 4 c.c. of the concentrated acid. It should be recalled that treatment with the acid frequently leads to the formation of a nitrate [*e.g.* $Ba(NO_3)_2$, $Pb(NO_3)_2$], which is difficultly soluble in the acid, but readily soluble in water. It is always best therefore, after heating the substance for some time with the acid, to decant the acid solution and to add some water to the residue, rather than to try to effect solution by using larger quantities of acid. If not more than 8 c.c. of the dilute or 4 c.c. of the concentrated acid have been used, the solution is diluted with water to 50 to 75 c.c. and is then ready for analysis according to **C, 20,** p. 100. If concentrated nitric acid is used or a large excess of the dilute acid, it is best to remove most of the excess of the acid, by evaporation in a porcelain dish, before going on with the analysis, as otherwise difficulties may develop in the treatment with H_2S. The residue, left by the evaporation, may then be dissolved in a little nitric acid (3 to 5 c.c.) and water (50 to 75 c.c.). The solution is then ready for analysis according to **C, 20,** p. 100.

17. Solution in Aqua Regia. — If the preliminary tests, made according to **12,** led to the selection of aqua regia as the proper solvent for the substance, or for any part of it not soluble in water, a gram of the substance, or the residue left when a gram of material has been previously extracted with water, is dissolved in as little aqua regia (3 parts of concentrated HCl and 1 part of concentrated HNO_3) as possible. If an insoluble residue is left, the solution is decanted from it and the residue examined as indicated in **18.** It should be borne in mind that the insoluble residue may have been produced by the action of the aqua regia (liberation of S, formation of AgCl, $PbCl_2$, $PbSO_4$ and other sulphates, etc.).

It is best to remove the excess of acid by evaporation, in a porcelain dish, on the steam bath, in order to avoid subsequent difficulties in the treatment of the solution with H_2S. Arsenic is oxidized by aqua regia to arsenic acid, which does not form a volatile chloride in aqueous solutions. The residue, left by evaporation, may then be dissolved in a little dilute hydrochloric acid (3 to 5 c.c.) and water (50 to 75 c.c.). The solution is then ready for analysis according to **C, 21,** p. 100.

18. The Substance is Insoluble or in Part Insoluble in water, hydrochloric acid, nitric acid and aqua regia. Any such insoluble part is analyzed as an "Insoluble Substance," for metal and acid ions, according to part **E,** p. 130.

II. *The Solution of a Metal or Alloy*

19. Treatment with Nitric Acid. — A gram of the metal or alloy is warmed with dilute nitric acid. If a crystalline salt separates, some water is added.

1. *A Clear Solution Results: Gold, platinum, tin* and *antimony* are *absent.* If not more than 10 to 15 c.c. of acid have been used, the solution is diluted with water to 50 to 70 c.c. and analyzed according to **C, 20,** p. 100. If more acid has been used, the acid is evaporated in a porcelain dish and the residue is dissolved in 4 to 5 c.c. of nitric acid and 50 to 75 c.c. of water and the solution analyzed according to **C, 20,** p. 100.

2. *A Dark Residue is left Undissolved:* This indicates the presence of *gold, platinum* or *carbon.*

(*a*) The *solution* is decanted and treated as directed in the preceding paragraph 1.

(*b*) The *residue* is washed with a little nitric acid, and, if it is *metallic*, it is dissolved in a little aqua regia, the aqua regia is evaporated and the residue tested for **gold** and **platinum** according to **26**, p. 105, and **28**, p. 106. If the dark residue is not metallic, or if the treatment with aqua regia left an insoluble black residue, the presence of **carbon** is indicated. Its identity may be confirmed by burning the residue on platinum foil, or on a porcelain crucible lid, heated to bright redness.

3. *A White Solid is left Undissolved:* Such a solid[1] usually consists of *stannic* and *antimonic* oxides, which may retain other oxides.

(*a*) The nitric acid solution,[2] with the solids suspended in it, is evaporated to dryness on the steam bath, the residue is dried 15 to 20 minutes at 120° and then treated with 4 or 5 c.c. of dilute nitric acid and 20 to 40 c.c. of water. The solution obtained is filtered and reserved for analysis according to **C, 20,** p. 100. A further small portion of solution may be secured in (*b*), which is to be added to this, before it is analyzed. The insoluble white residue (of antimonic or stannic oxides) is treated as follows:

(*b*) The white residue is washed with a little water and dilute nitric acid and then digested with ammonium persulphide (yellow ammonium sulphide). *Stannic* and *antimonic* oxides (and any retained *arsenic* acid) dissolve in the form of ammonium salts of their sulpho-acids; *other metal oxides*, that may have been retained by the acid oxides, are left *undissolved* in the form of sulphides. The latter are washed with a little ammonium sulphide and then dissolved in a little warm dilute nitric acid. This solution is added to the solution obtained above in (*a*) and the whole analyzed according to **C, 20,** p. 100. The ammonium sulphide solution, which may contain tin, antimony or arsenic, is reserved until the analysis of the nitric acid solution has reached the point (**22**), where the arsenic group of sulphides is dissolved in ammonium sulphide. The two ammonium sulphide solutions are then united and analyzed according to **24,** p. 105, for the arsenic group.

---

[1] If it is flocculent rather than pulverulent in appearance, it probably is *silicic acid*. In that event consult *Fresenius*, p. 444, in regard to the method of treatment.

[2] The method of treatment is that recommended by Böttger, *Qualitative Analyse*, p. 429.

C. THE ANALYSIS FOR METAL IONS OF SUBSTANCES SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID OR AQUA REGIA[1]

I. The Precipitation of the Silver Group by HCl

20. The solution[2] (read footnote 2 carefully) is treated with a small excess of HCl, unless it already contains this acid.

If no precipitate is formed within five minutes, proceed, with a nitric acid solution of the unknown, directly to **21,** with an aqueous solution, to **21,** after adding to it 4 c.c. of hydrochloric acid.

If a precipitate is formed by the addition of the first 5 or 6 drops of the acid, continue adding the acid slowly, until no further precipitate is seen to form when the mixture is shaken, the precipitate allowed to settle and a drop or two of acid is added to the clear supernatant liquid. Then add an excess[4] of 2 or 3 drops of the acid, to an acid (nitric) solution, an excess[3] of 3 c.c., to an aqueous solution of the unknown.

A *precipitate* is collected on a filter, washed twice with 5 c.c. of water and examined for **lead, silver** and **mercurous chlorides** according to p. 48, section II.

The *filtrate,* including the washings, is treated according to **II, 21,** which follows.

II. The Precipitation of the Arsenic and Copper Groups by H_2S

21. 1. It should be recalled that the successful precipitation of sulphides in acid solutions depends on certain precautions as to the concentration of the hydrogen-ion in the acid solution (see Chapter XI), and that the precipitation of arsenic as the sulphide, when the arsenic is present as *arsenic acid*, takes place *extremely* slowly in the cold, but more readily at 70° to 80°. To insure complete precipitation of all the sulphides of the copper and arsenic groups, the directions in §§ 2 to 4 should therefore be carefully observed.

---

[1] In entering results observed, *record carefully whether a component, that has been found, is present in large or small proportions or in traces only.* Solutions and precipitates should be treated as a whole, unless specific instructions to the contrary are given, and, in the latter case, the division of the material should be taken into account in judging the quantities present.

[2] The solution has been prepared according to **11,** p. 93, if the original substance is a liquid; according to **12** to **17,** if it is a nonmetallic solid; according to **19,** if it is a metal or alloy. *Particular attention* must be paid to the preparation of a liquid with an *alkaline reaction* (**11,** 3) or of an aqueous solution of a solid, which shows an *alkaline reaction* (**13**).

[3] This prepares the solution for the precipitation with H_2S.

[4] The excess redissolves any precipitated (BiO)Cl or (SbO)Cl.

If a precipitate or precipitates are obtained with H_2S in carrying out the directions in §§ 2, 3 and 4, *the combined precipitates are examined according to* **22** *for the presence of the arsenic and copper groups; the filtrate*, freed from the metal ions of these two groups, is boiled, to remove the H_2S, and *is reserved for analysis for the zinc and aluminium groups*, **VI, 33,** p. 107. *If* H_2S *fails to give any precipitate* at all, or forms only a white precipitate of sulphur,[1] the *solution is examined at once according to* **VI, 33,** p. 107, *for the zinc and aluminium groups.*

2. *Pass* H_2S *into the cold solution to saturation.*[2] *If no precipitate is formed*, proceed as directed in §§ 3 and 4 below. A *precipitate* (sulphides of the copper and arsenic groups) is collected on a small filter, washed with 10 c.c. of hydrogen sulphide water[3] and immediately covered with a beaker, inverted over the funnel. The filtrate is treated according to § 3 and then according to § 4, which follow.

---

[1] The formation of sulphur indicates the reduction of some component of the solution (*e.g.* Fe^{+++}, Cr^{++++++}, $Mn^{+++++++}$) by the sulphide-ion.

[2] The precipitation should be carried out in an Erlenmeyer flask of 120 to 150 c.c. capacity. The flask should be fitted with a double-holed stopper, through one hole of which the delivery tube, bent at right angles, passes, ending near the bottom of the flask. Through the other hole a short exit tube, also bent at right angles, passes; a short piece of rubber tubing, carrying a pinch clamp, is attached to the exit tube. A rapid stream of H_2S is passed through the solution, the pinch clamp being open at first, so that the air in the flask is expelled. Then the clamp is closed and the solution is saturated with the gas. Occasionally the clamp should be opened, for a few moments, to allow any air to be expelled, that may enter the flask from the generator. *If the air is expelled* in this way and the current from the generator stops a few moments after the clamp is closed, the solution is saturated with the gas.

[3] If the washings are cloudy (colloidal suspension), add a gram or two of ammonium nitrate to them and refilter them. Any subsequent washing of the precipitate (see below) should then be made with hydrogen sulphide water containing 5 to 10 per cent of ammonium nitrate.

3. In order to insure the precipitation of *arsenic*, if present in the form of *arsenic acid*, H_2S is passed, at 70°–80°, into the filtrate (with washings), obtained in § 2, or into the solution[1] in which H_2S failed to produce a precipitate in the cold. The treatment at 70°–80° must be continued at least 10 to 15 minutes, before the *absence* of a *precipitate* may be considered to indicate the *absence* of *arsenic* in the pentavalent form.

(*a*) *If no precipitate forms*, pass on to § 4.

(*b*) If a *yellow precipitate forms*, the presence of *arsenic* in the pentavalent form of arsenic acid is indicated. The treatment with H_2S, at 70°–80°, is continued for 10 or 15 minutes more, the mixture is *cooled* and the precipitate is collected on the same filter on which any precipitate obtained according to § 2 has been collected. The *precipitates* are washed with 10 c.c. of hydrogen sulphide water and carefully covered as described in § 2. The *filtrate* is examined according to § 4.

4. The filtrate (with washings), obtained from any precipitates formed by H_2S in the cold or at 70° to 80°, or the solution in which H_2S failed to produce a precipitate, is still to be tested so as to *insure the precipitation of* metal sulphides (CdS, PbS, etc.), *whose precipitation* by H_2S *may have been prevented* by too great a concentration of the hydrogen-ion in the solution. This is particularly necessary, if the solution of the original substance required concentrated acids or a large excess of the dilute acids.

Dilute the solution to 100–120 c.c. and test the concentration of the acid (hydrogen-ion) by adding a drop of the diluted solution, by means of a glass rod, to a methyl violet mark[2] on a piece of sized paper (see the directions in the footnote on p. 31), or by adding, with a pipette, 0.1 c.c. of the diluted solution to 0.1 c.c. of methyl violet solution, on a white tile or crucible lid.[3] A *blue-green* or blue tint, produced in either test, shows that the concentration of hydrogen-ion is now not too great for the precipitation, without particular difficulty, even of minute quantities of the metal sulphides mentioned. A *yellow-green* or *yellow tint* shows that there is too great an excess of acid present.[1]

---

[1] The apparatus described in footnote 1 is used, but the clamp must be left *open*.

[2] A concentration corresponding to 0.1 molar HCl produces a pure blue stain, 0.25 molar HCl a blue-green stain, 0.33 molar HCl a yellow-green stain, and 0.5 or stronger HCl a yellow stain. *Consult*, also, *footnote 1*, p. 103.

[3] The tints indicate the same concentrations as given in footnote 1.

(*a*) *If the concentration of hydrogen-ion is not too great* (*blue* or *blue-green* tint of the indicator), saturate the solution with H_2S in the cold and let the mixture stand 15 minutes. A yellow precipitate indicates cadmium, a black one lead (in which cadmium may be masked), a brown one tin or lead or a mixture of lead, tin or cadmium. Any such *precipitate* is collected on a small filter, washed with 5 c.c. of H_2S water and added to the remainder of the sulphides which may have been precipitated in § 2 or § 3.

(*b*) *If the concentration of hydrogen-ion is too great* (*yellow* or *yellow-green* tint of the indicator), the solution is evaporated to dryness, the residue is dissolved, with the addition of 4 c.c. of dilute HCl, in 100 c.c. of water and the solution treated as described in (*a*) (the preceding paragraph).

III. The Separation of the Arsenic and Copper Groups by $(NH_4)_2S$ and $(NH_4)_2S_x$

22. *A small portion of the* **sulphides, precipitated by H_2S** *according to* **21,** is tested to see whether both the *copper* and the *arsenic groups* or only one is present: it is warmed with 3 to 5 c.c. of light-yellow ammonium sulphide. We distinguish three cases.

1. *Complete solution* insures the **absence** of the **copper group.**[2]

---

[1] The blue-green tint of 0.25 molar HCl indicates the average maximum desirable concentration of hydrogen-ion in ordinary work. Even a trace of CdS *may be precipitated* in the presence of somewhat more concentrated solutions of the hydrogen-ion, but so slowly and difficultly that it is preferable not to exceed this limit. For instance, 1 milligram Cd^{++} gave a plain yellow precipitate in 2 *to* 3 *minutes* in 100 c.c. solution containing 0.25 molar HCl; in a similar solution containing 0.33 molar HCl a faint yellow cloud was formed in about 3 minutes and a precipitate in 10 to 15 minutes; but a solution of 1 milligram Cd^{++} in 100 c.c. 0.5 molar HCl gave no precipitate in 15 minutes, and only after standing 30 minutes (altogether) was a plain precipitate observed. See also Noyes and Bray, *J. Am. Chem. Soc.*, **29,** 1С7 (1907). Mercuric chloride precipitates methyl violet and would interfere with the test: HgS, however, is precipitated even in the presence of a large excess of acid, and the chloride is thus decomposed before the test is made.

[2] See, however, p. 42, as to the loss of a trace of *copper*. It can be found by solution of the arsenic group sulphides in sodium sulphide. A residue is collected, washed and treated with a drop of nitric acid, and the solution tested for copper (p. 51, §§ 2 and 3). The arsenic group sulphides are reprecipitated, by acid, and analyzed (**24,** p. 105).

If the copper group is *absent*, the whole of the sulphide precipitate is analyzed according to **V, 24**, p. 105, for the **arsenic group** of metals.

2. *A colored residue* is left. The **copper group** is **present.** The solution is filtered from this colored residue, and hydrochloric acid, in excess, is added to the filtrate: a pure white precipitate is *sulphur* from the ammonium sulphide.[1] Benzene may be added to the mixture: if only a *whitish residue* is left, the **arsenic group is absent** and the whole quantity of the precipitated sulphides is examined only for the metals of the copper group, according to **IV, 23,** below.

3. *A colored residue* is left and hydrochloric acid, added to the *ammonium sulphide filtrate*, gives *a colored precipitate.* **Both the copper and the arsenic groups are present.**[2] The whole quantity of the precipitated sulphides is extracted twice with somewhat darker yellow ammonium sulphide (to insure the solution of stannous and antimonous sulphides), the undissolved **residue** is analyzed for the **copper group** metals according to **IV, 23,** below; the filtrate is acidified with hydrochloric acid, the reprecipitated sulphides of the **arsenic group** are brought on a filter, and analyzed according to **V, 24.**[3]

IV. The Analysis of the Copper Group

23. Analyze the precipitate, obtained according to **22,** 2 or 3, for **mercury, lead, bismuth, copper** and **cadmium** according to pp. 50–52, section III, §§ 2 and 3, and section IV.

---

[1] Treat a few drops of light-yellow ammonium sulphide with water and hydrochloric acid for a comparative test.

[2] If only a *slight brownish precipitate* is formed by the hydrochloric acid, this may be cupric sulphide, which is, as stated, slightly soluble in ammonium sulphide. In such a case, before deciding that the arsenic group is present, collect the slight precipitate on a filter and treat it with a drop or two of sodium sulphide solution. Cupric sulphide is left undissolved; the sulphides of the arsenic group dissolve. Dilute the solution, filter it, if CuS is left, and acidify the filtrate. A *colored precipitate* (even slightly yellow) indicates that the *arsenic group* is present. Proceed then according to § 3. If the precipitate proves to be only a trace of CuS, proceed according to § 2.

[3] If the precipitate is to be examined for a *trace* of *copper*, as is necessary, in exact work, if copper is not found in **IV, 23,** it is first treated with sodium sulphide in excess, and the cupric sulphide and the sulphides of the arsenic group are recovered as described in footnote 2, p. 103.

V. The Analysis of the Arsenic Group[1]

24. The **sulphides** of the **arsenic group,** obtained according to **22,** 1 or 3, are freed on the filter, as far as possible, from adhering water, by suction with the filter pump. They are heated in a test tube with exactly 10 c.c. of concentrated *hydrochloric acid* (*sp. gr.* 1.2, *side shelf*), the mixture being brought almost to 100°, by immersion for ten minutes in a beaker full of boiling water; 5 c.c. of water are added to the solution, the latter is filtered (filtrate **F**), and the residue **R** washed once with 5 c.c. of water, the washing being added to the filtrate **F**. The filtrate **F,** containing any **antimony** and **tin,** which may have been present, is diluted with 30 c.c. more of water and reserved for analysis according to **29** or **30.** The residue **R,** which may contain **arsenic, gold** and **platinum** (and sulphur), is washed with dilute hydrochloric acid to remove the last traces of antimony and tin, and then analyzed according to **25.**

25. If **gold** and **platinum** are to be considered, the residue **R** is analyzed according to **26**; if they are not to be considered, it is tested only for **arsenic** according to p. 62, § 2 (molybdate test or cyanide test).

26. If **gold** and **platinum,** as well as **arsenic,** are to be considered, the residue **R,** obtained in **24,** is warmed in a porcelain dish with 5 to 10 c.c. of dilute hydrochloric acid, and solid potassium chlorate is added, in *small portions,* until the oxidation of the sulphides is complete. Any sulphur is filtered off and the solution (S) concentrated to about 2 c.c. If the solution is yellow, or if a yellow precipitate (K_2PtCl_6) has formed, **platinum** is indicated. If it is colorless proceed to **27**; if it is yellow, the solution S is further concentrated until potassium chloride crystals appear, then the yellow *potassium chloroplatinate* is collected on a very small filter and washed with a cold saturated potassium chloride solution. The filtrate is reserved for **27.** (Why is K_2PtCl_6 less soluble in KCl solution than in water?) The precipitate is dissolved in a few cubic centimeters of hot water and treated with a few drops of potassium iodide solution; a deep-red solution, K_2PtI_6, or black precipitate, PtI_4, confirms **platinum.**

---

[1] *Cf.* A. A. Noyes and Bray, *Technology Quarterly,* 1906, and *J. Amer. Chem. Soc.,* **29,** 176 (1907).

27. The filtrate from the potassium chloroplatinate, or the *colorless solution* S obtained in **26,** is rendered alkaline (test) with ammonium hydroxide, the cooled solution is filtered, if necessary, any precipitate (antimony or stannic hydroxides) being rejected; a cubic centimeter of magnesium nitrate mixture and one-third of a volume of concentrated ammonium hydroxide are added to the clear filtrate to precipitate magnesium ammonium *arseniate.* If no precipitate forms immediately, rub the walls of the test tube gently with a glass rod for a minute or two, as crystallization is often delayed. A precipitate shows the presence of **arsenic.** If there is no precipitate proceed to **28.** A precipitate is collected on a very small filter, washed once with concentrated ammonium hydroxide, the filtrate **FF** being reserved for **gold** tests given in **28,** and the *arseniate* precipitate dissolved in a little dilute nitric acid. A portion of this solution, boiled with four or five volumes of molybdate solution (*nitric acid solution*),[1] should give a yellow precipitate of ammonium *arseno*-molybdate (p. 54, § 3 (*c*)), confirming **arsenic**; a second portion, when treated with silver nitrate, filtered from any precipitated silver chloride, and covered with a layer of dilute ammonia, should show a brown ring of silver *arseniate.*

28. The filtrate **FF,** separated from the magnesium ammonium arseniate in **27,** or the solution in which magnesium nitrate mixture failed to precipitate any arseniate, is treated with 2 to 3 c.c. of saturated oxalic acid solution, and the mixture evaporated to 3 to 4 c.c., to expel the excess of ammonia. The residue is made slightly acid with oxalic acid, diluted to 15 c.c. and heated on a steam bath for several minutes. A purple precipitate shows **gold.**

29. The filtrate **F** of **24** must still be tested for **antimony and tin.** The tests may be carried out as on p. 62, § 3, by the method of reduction with a steel nail or with tin and platinum. In testing for tin with mercuric chloride, the acid solution must be considerably diluted, as mercurous chloride is soluble in strong hydrochloric acid.

The following method,[2] given in **30,** may be used instead.

---

[1] If an ammonium molybdate solution without nitric acid is used, *the reagent is treated with an equal volume of nitric acid before it is used.* The addition of some ammonium nitrate (about a gram to 10 c.c.) increases the sensitiveness of the reagent.

[2] Noyes and Bray, *loc. cit.*

30. The filtrate **F,** as obtained in **24,** is heated in a test tube, placed in a beaker of hot water (90°), and treated with hydrogen sulphide gas for five minutes. If no precipitate (*antimony* sulphide) forms, add 5 c.c. of water and treat the solution again with hydrogen sulphide at 90°. An orange-red precipitate indicates **antimony.** (In the cold, tin sulphide could be precipitated.) 5 c.c. of water should be added once more and the treatment repeated to insure complete precipitation of the *antimony.* The filtrate, or the solution in which no precipitate was formed, is examined for **tin** according to **32,** the precipitate of **antimony** sulphide is examined according to **31.**

31. The sulphide precipitate, obtained in **30,** is dissolved in very little concentrated hydrochloric acid, the solution evaporated to 1 c.c. and then treated with some pure tin, placed on platinum foil; a black deposit on the platinum indicates **antimony.** It is washed well with water and then treated with some sodium hypochlorite (extract 0.3 to 0.5 gram chloride of lime with 3 c.c. of water, add sodium carbonate, in slight excess, to the filtered extract, and filter the solution of sodium hypochlorite from the precipitated calcium carbonate). **Antimony** does not dissolve, arsenic, if present, would dissolve.

32. The filtrate from the antimony sulphide, obtained in **30,** is examined for **tin** as follows: a portion is diluted with water and treated with hydrogen sulphide in the cold; a yellow precipitate (tin sulphide) indicates **tin.** A second portion is boiled to remove hydrogen sulphide and then treated with an iron nail for ten to twenty minutes; and the solution is then tested with mercuric chloride: a white precipitate of mercurous chloride, or a gray one of mercury, proves the presence of **tin** (p. 57, § 2).

VI. The Zinc and Aluminium Groups (*and possibly the* Alkaline Earths, *as Phosphates, Borates, Fluorides, Oxalates, etc.*)

33. To appreciate the requirements for a correct course of analysis of the solution remaining after the removal of the silver, copper and arsenic groups, the student must consider, in particular, the two following points:

1. He must first recall the fact that certain *organic substances,* like tartrates, citrates, sugar, etc., interfere with the precipitation of hydroxides, phosphates, etc. (p. 83, § 2 (*b*) and Chapter XII,

p. 238); since aluminium and chromium are to be precipitated as hydroxides, the alkaline earths as phosphates or carbonates, organic matter of the above nature, if present, must be *destroyed* before the further analysis is made. *All these organic compounds char on being heated* (p. 88, **2**). *A small portion of the original unknown is tested* in this way for organic matter, if the test has not been made before (p. 87, **1**).

(*a*) If *organic* compounds *are present*, and particularly if charring occurs or the odor of burnt sugar (sugar, tartrates) is developed when the original unknown is heated in a glass tube (p. 88, **2**), the organic matter must be destroyed before the analysis is continued. About one-fourth of the solution which is to be examined (see p. 101, § 1), is reserved for the examination for sodium and potassium according to **VIII 44** (p. 115). The remainder is evaporated in a platinum dish (Instructor), an equal part of dry sodium carbonate and a little potassium nitrate are mixed with the dried residue, and the mixture is gently heated until the organic matter is destroyed. The mass is extracted with hydrochloric acid in excess, and the extract analyzed according to **34**, p. 109 (but first read the following § 2).

(*b*) In the *absence of organic matter* proceed to **34**, p. 109, after reading § 2, which follows.

2. The *second complication*, that the student must consider, is the fact that whereas ammonium hydroxide and sulphide, in the presence of ammonium chloride, will not precipitate a *sulphide* or *hydroxide* of the alkaline earths — as these are sufficiently soluble — they may, under certain conditions, precipitate *insoluble salts* (e.g., *phosphates, fluorides, oxalates*, etc.) of the *alkaline earths*. These would then be mixed with the hydroxides and sulphides of the zinc and aluminium groups, and, unless they were considered, they might be entirely overlooked. For instance, if the original unknown contained barium phosphate, hydrochloric acid, in excess, would have been used as solvent. When ammonium chloride and ammonium hydroxide are added to the solution for the precipitation of the zinc and aluminium groups, the barium phosphate would be reprecipitated. We have

$$Ba_3(PO_4)_2\downarrow + 6\,HCl \rightarrow 3\,BaCl_2 + 2\,H_3PO_4 \qquad (1)$$

$$\begin{gathered}3\,BaCl_2 + 2\,H_3PO_4 + 6\,NH_4OH \rightarrow \\ 3\,BaCl_2 + 2\,(NH_4)_3PO_4 + 6\,H_2O \rightarrow \end{gathered} \qquad (2)$$

$$Ba_3(PO_4)_2\downarrow + 6\ NH_4Cl + 6\ H_2O \qquad (3)^1$$

(Why does *ammonium phosphate* precipitate barium phosphate (equation (3)), when phosphoric acid does not (equation (1))?

Considering (1), (2), (3), it is evident that *this complication* will only be *possible*, when the *original solution* of the unknown (see the above equation (1)) is *not neutral* (usually only when it is *acid;* when it is alkaline, only in the presence of organic matter), **and** when *ammonium hydroxide precipitates a solid* even *before* the addition of *ammonium sulphide.* If *both* of these conditions are fulfilled, alkaline earths *may* come down in the zinc and aluminium groups, otherwise not. In the first event, the analysis for the zinc and aluminium groups is modified to include tests for the alkaline earths. An acid solution and precipitation by ammonium hydroxide may, however, be due to the presence also of *other* metal salts (*e.g.* ferric chloride or nickel phosphate, etc.).

34. The Process of Analysis, based on the above considerations, is the following: In the absence of organic matter, [or after its removal, if present (see 33, 1 (*a*))], a *small portion* (about 5 c.c.) of the solution which has been freed from the arsenic, copper and silver groups (in 20 and 21), or of the solution in which these groups have been found to be absent (in 20 and 21), is boiled to remove H_2S and CO_2. Add to the boiled solution a few drops of bromine water (to convert ferrous into ferric iron), and boil the solution to remove the excess of bromine. Cool the solution, add 4 or 5 c.c. of *ammonium chloride* solution and enough *ammonium hydroxide* to make the reaction of the solution *alkaline* to litmus. We distinguish three cases, 1, 2 and 3.

1. (*a*) *No precipitate is formed by ammonium hydroxide,* even in the course of a few minutes: **aluminium, chromium** and **iron** *are absent,* as well as phosphates, borates and other insoluble salts of alkaline earths.

(*b*) Add *ammonium sulphide* to the solution in which ammonium hydroxide failed to give a precipitate. *If no precipitate is formed,* **nickel,**[2] **cobalt, manganese** and **zinc** *are absent.* The main solution, together with the small portion taken for the test, is examined according to **41,** p. 114, for the *alkaline earth group.* A *precipitate,*

---

[1] The secondary phosphate, $BaHPO_4$, may also be precipitated.

[2] Examine a *brown* solution for a trace of **nickel** (p. 36, I, § 2).

formed by ammonium sulphide, may contain **nickel, cobalt, manganese** and **zinc**. If such a precipitate is produced, the whole of the main solution,[1] including the small portion taken for the test, is treated with 10 c.c. of *ammonium chloride* solution, with sufficient *ammonium hydroxide* to render the mixture just alkaline,[2] and with a small excess of *ammonium sulphide*, and the mixture is warmed. The *precipitate* is collected on a filter, *washed well* with water, to which a little ammonium sulphide and some ammonium chloride or nitrate have been added. It is analyzed for **nickel, cobalt, manganese** and **zinc** according to p. 40, **V**, § 3.

(*c*) The *filtrate from the sulphides* is immediately[3] treated with sufficient acetic acid to render it slightly acid, boiled to remove hydrogen sulphide, and filtered from the precipitated sulphur.[4] It is then *reserved for analysis* according to **41** (p. 114).

2. *Ammonium hydroxide forms a precipitate*, but the *original solution* of the unknown was *neutral*. In this case the phosphates and other insoluble salts of the alkaline earths are again absent. Proceed as in 1 (*b*), but make a complete analysis of the *precipitate* for the ZINC and ALUMINIUM GROUPS, p. 35, I–V. The *filtrate* from the precipitate is treated, at once, as described in 1 (*c*), above.

3. *Ammonium hydroxide forms a precipitate* and the *original solution* of the unknown *was not neutral*. Treat the whole of the main solution, including the portion taken for the preliminary test, with *ammonium chloride, ammonium hydroxide* and an excess of *ammonium sulphide*, as described above in 1 (*b*). The *precipitate* is collected and washed as described in 1 (*b*), and analyzed according to the directions, which follow below: the *filtrate* from the precipitate is treated, at once, as described in 1 (*c*), above.

The *precipitate* may contain all the metal ions of the zinc and aluminium groups, as well as the alkaline earth ions (as phosphates, etc.) It is treated, according to its bulk, with 50 to 150 c.c. of *diluted* hydrochloric acid (1 part dilute acid and 4 parts of water), which is allowed to act for three to five minutes. A residue **R,** which should be washed well, is analyzed according to **35,** and the filtrate **F** is analyzed according to **36, 37,** etc.

---

[1] If the original substance contained a carbonate (effervescence with acids, limewater test), the acid solution, if it has not been boiled before, must be boiled to remove CO_2, before ammonium hydroxide is added to it; otherwise alkaline earth carbonates would be precipitated.

[2] A greater excess of ammonium hydroxide is to be avoided on account of its action on aluminium hydroxide (Chap. X, p. 196), when present.

[3] This treatment is intended to prevent absorption of oxygen and carbonic acid from the air, which would precipitate sulphates and carbonates of the alkaline earths. *Cf.* Baskerville and Curtman, *Qualitative Analysis* (1910).

[4] If acetic acid produces a *dark* precipitate in a *brown* solution, it is collected, before the mixture is boiled, and tested for **nickel** (p. 36, I, § 2).

35. A *black* residue **R** probably contains **nickel** or **cobalt** or both. It may also contain **calcium fluoride** and **silicic acid,** if a silicate decomposable by acid was originally present and its presence overlooked in the preliminary test discussed in **1.** If the residue **R** is *white,* it consists of sulphur or contains **silicic acid** or **calcium fluoride.**

1. If the residue **R** is *black,* examine about one-half of it for **nickel** and **cobalt** according to II, p. 36, modified as follows:

In the evaporation with hydrochloric and nitric acids (II, § 2, p. 36) evaporate the solution to dryness, dry the residue ten minutes at 120°, warm it with 3 or 4 c.c. of hydrochloric acid, and test the solution, formed, for **nickel** and **cobalt.** If a white residue is left undissolved, which is not light and combustible (sulphur), **silicic acid** is indicated: it is confirmed by the metaphosphate or SiF_4 tests, pp. 69–70. Another portion of the residue **R** is warmed with a few drops of concentrated sulphuric acid, the liquid is cooled, diluted with 4 or 5 volumes of water, the solution filtered and treated with three volumes of alcohol. Confirm a white precipitate as **calcium** sulphate, after it is collected and washed, by dissolving it in water and treating the solution with ammonium oxalate. In the presence of calcium, mix the remainder of **R** with some silica, and test it for fluorides by the SiF_4 test, p. 70. In the absence of calcium, the test is omitted. If the white residue is very slight, the test for fluoride and calcium should be combined, the fluoride test being made first.

2. If the residue **R** is *white* and not completely combustible (sulphur), it is tested for **silicic** acid and **calcium fluoride** according to § 1, and the nickel and cobalt tests are omitted.

36. A *small portion* (one-tenth) of the filtrate **F** is boiled, to remove H_2S, almost neutralized with ammonium hydroxide, and treated with a few drops of sulphuric acid, as long as a precipitate forms.

1. An *immediate precipitate* proves **barium,** a more slowly formed precipitate is probably **strontium** sulphate. It is collected, washed, and examined, with the flame, for these metals (p. 15, § 11). A little of the precipitate is heated in the reducing flame, to convert the sulphates into sulphides, the mass is then treated with a drop

of hydrochloric acid and heated in the edge of the flame; there is usually no difficulty in recognizing **barium** and **strontium**, side by side, in this way, as the flame colorations follow each other. The flame may also be examined with the aid of the spectroscope. For a more exhaustive analysis, the sulphates are fused with a mixture of sodium and potassium carbonates, and the mass extracted with water, to remove the sodium and potassium salts; the carbonates of the alkaline earths are then dissolved in nitric acid and the solution examined according to method A, p. 17, for barium and strontium, or the carbonates are dissolved in acetic acid and the solution analyzed according to method B, p. 20.

2. The *filtrate from the sulphates* or, if no sulphate was precipitated, the solution to which sulphuric acid was added, is treated with three volumes of alcohol, to precipitate **calcium** sulphate. If a precipitate is obtained, it is collected on a filter, washed with alcohol, shaken with a little water, and an excess of ammonium oxalate added to the solution: an immediate precipitate confirms the presence of **calcium.** Without this confirmation calcium must not be reported.

37. The major portion of the filtrate **F** (**34,** § 3) is heated to remove hydrogen sulphide, and treated with an excess of bromine water to convert any ferrous into ferric salt;[1] the excess of bromine is boiled away, and a little (1 to 2 c.c.) of this solution S tested with ammonium thiocyanate for **iron.** If iron is found, its original form, as **ferrous** or **ferric** iron, or both, is determined by examining the original unknown: the thiocyanate or the ferrocyanide test is used to detect ferric-ion, p. 29, § 5; the ferricyanide test is used to detect ferro-ion (1 (*b*), p. 32). In order to avoid oxidation of the latter in effecting the solution of the substance, the solution may be made in an atmosphere of carbon dioxide, by the addition of some sodium bicarbonate and hydrochloric acid to the substance, while it is dissolving.

38. Irrespective of the presence or absence of iron, ferric chloride[2] is added to the main part of the solution S (obtained in

---

[1] Evidence that the oxidation is complete may be obtained by testing a drop of the mixture with a drop of ferricyanide solution, on a white surface; as long as a *blue* precipitate is formed, ferrous salt is still present.

[2] Ferric chloride is added to separate phosphoric acid from magnesium, which may be present. The acid solution S could contain magnesium chloride,

37), until a drop of the mixture, when tested with ammonium hydroxide, gives a *reddish* precipitate. Then sodium carbonate is added until a *slight permanent* precipitate is formed. This is redissolved *in as little hydrochloric acid* as possible, and aluminium, chromium and iron are precipitated by barium carbonate in the cold, according to III, § 2, p. 38. The precipitate is tested for **aluminium** and **chromium** according to IV, § 1 or § 2, p. 38. Examine the filtrate **FF** for *manganese* and *zinc*, traces of *cobalt* and *nickel*, and for *magnesium*, according to **39** and **40.**

39. Add 1 or 2 c.c. of hydrochloric acid to the filtrate **FF,** obtained in **38,** and concentrate the solution to a volume of 10 to 15 c.c. Then add 3 to 5 c.c of ammonium chloride solution, sufficient ammonium hydroxide to render the solution alkaline and a small excess of ammonium sulphide, and warm the mixture for a few minutes. A *precipitate* could contain **manganese, zinc** and small quantities of **nickel** and **cobalt;** the precipitate is collected on a filter and examined for the ions of these metals according to V, p. 39. The *filtrate,* or the solution, in case ammonium sulphide gave no precipitate, is examined for *magnesium* according to **40.**

40. The filtrate from the manganese, zinc (nickel and cobalt) sulphides, or the solution in which they were found to be absent, must still be examined for *magnesium.* It is heated to boiling, and treated with sulphuric acid, as long as barium sulphate is formed; the liquid is *cooled,* and, without filtration, ammonium hydroxide, ammonium oxalate and ammonium carbonate are added, to remove calcium and strontium. The solution is filtered from these precipitates, the filtrate is concentrated and tested for **magnesium** with ammonium hydroxide and sodium phosphate (p. 8, § 3). Crystallization is often delayed. If a precipitate is not formed, rub the test tube gently with a glass rod.

ammonium chloride and phosphoric acid, if magnesium and phosphate ions were in the original solution of the unknown. After the addition of an excess of ferric chloride, when the solution is neutralized, ferric phosphate is precipitated: $MgCl_2 + NH_4Cl + FeCl_3 + Na_3PO_4 \rightarrow MgCl_2 + NH_4Cl + FePO_4\downarrow + 3\,NaCl$. Magnesium chloride is in solution. Why is ferric phosphate precipitated in preference to magnesium-ammonium phosphate? Precipitate some ferric phosphate and some magnesium-ammonium phosphate, separately, and add acetic acid to each. Does the experiment confirm your conclusion?

VII. The Analysis of the Alkaline Earth Group

41. The solution from which the silver, arsenic, copper, zinc and aluminium groups have been removed is examined according to pp. 17 to 22, for **barium, strontium, calcium** and **magnesium,** regard being taken of the possible presence of traces. Either method A or method B may be used. If organic matter of the type of tartaric acid or sugar is present in the original substance, this organic matter must have been destroyed, according to **33,** 1 (*a*), before the examination for alkaline earths is carried out.

The *filtrate* from the precipitated alkaline earth carbonates and from any precipitated magnesium-ammonium phosphate (method A, p. 18), or the filtrate from the alkaline earth carbonates (including magnesium) (method B, p. 20), is analyzed for **sodium** and **potassium** according to **43,** if organic matter is absent, according to **44,** if organic matter is present.

VIII. The Analysis of the Alkali Group

42. The original unknown is tested for **ammonium** ion according to p. 3, § 2 (*a*).

43. In the *absence of organic matter*, the filtrate from the alkaline earths, obtained according to **41,** is evaporated to dryness, the ammonium salts are removed *completely* by gentle ignition of the solids, in a porcelain dish, until neither white fumes (solid ammonium salt particles) nor ammonia gas (litmus test) are any longer formed. Any residue is dissolved in as *little* water as possible; usually 1 to 2 c.c. will be sufficient. The residue may be found difficultly soluble in water and glassy, if ammonium phosphate was used in precipitating magnesium-ammonium phosphate (method A for the alkaline earths): the metaphosphates, formed on ignition, are difficultly soluble in water. In the event that such a residue is obtained, heat it[1] with 1 c.c. of concentrated hydrochloric acid for a few minutes, evaporate the acid on the steam bath and dissolve the new residue in as little water as possible.

1. A drop of the *aqueous solution* is held in the loop of a clean (test?) platinum wire in the flame; if a **sodium** flame is obtained,

---

[1] Dissertation by H. R. Smith for the M.S. degree, University of Chicago, 1910. The treatment with 1 c.c. of acid is sometimes advantageously repeated once.

the flame is observed through a piece of cobalt glass for the presence of **potassium.**

2. A small portion of the solution is then tested (without dilution) for **potassium** with chloroplatinic acid[1] (p. 4, § 4), the mixture being evaporated to dryness and the residue taken up with a drop or two of water, if the test should at first prove negative; or the test for **potassium** may be carried out (without dilution) with sodium cobaltinitrite solution (p. 4, § 5).

3. Another portion of the solution is tested for **sodium** with the solution of potassium pyroantimonate, according to § 6, p. 4.

44. In the *presence* of *organic* matter, the solution reserved in **33,** 1 (*a*), p. 108, for the determination of the alkalies, is evaporated to dryness in a porcelain dish. The residue is carefully moistened with pure concentrated sulphuric acid and the mixture gently heated, until most of the acid is expelled. The residue is extracted with water, the solution heated, and the metals of the zinc and aluminium groups precipitated by means of ammonium chloride, ammonium hydroxide and ammonium sulphide, the alkaline earths by means of ammonium carbonate and ammonium phosphate; the filtrate from the mixed precipitate is analyzed according to **43.**

D. THE ANALYSIS FOR ACID IONS OF SUBSTANCES SOLUBLE IN WATER, ACIDS OR AQUA REGIA

Introductory. In the acid tests used in the directions that follow, emphasis is placed on those that are carried out in *acid* solutions, since metal ions, other than the alkali ions, are likely to interfere with tests made in neutral or alkaline solution (see Chapter XVI). Such metal ions may, however, be removed, and the acids obtained in the form of *sodium salts,* by proper treatment, with sodium carbonate, of the substance to be analyzed. In **49,** directions are given for the preparation of a *nitric acid solution* for analysis; in **50,** directions are given for the preparation of a solution of *sodium salts.* Students should become familiar with both methods of analysis; the indications for using the one or the other are given in **48.**

---

[1] Iodide-ion interferes with the chloroplatinic acid test for potassium, forming a red solution of Me_2PtI_6 or a black precipitate, PtI_4. Treatment of the iodide with a few cubic centimeters of aqua regia, which is subsequently evaporated, will overcome the difficulty. By using the cobaltinitrite test, the difficulty is avoided.

In **45–47** the acids which are usually detected in the course of the analysis for metal ions are considered first.

If the substance is insoluble in water or acids (p. 98, **18**), *it is analyzed according to Part* **E**, *p.* 130.

The metal ions having been determined, *the solubility of unknowns in water or acid will usually serve to shorten the course of analysis for the acids* very considerably. *The Table of Solubilities on pp.* 140–1, *should be consulted.* Do not look for acid ions whose presence is *incompatible* with observations made in the analysis for metal ions. Thus a *calcium* salt, soluble in *water* with a *neutral* reaction, cannot be a *phosphate.* (See table, p. 140.) But if it is soluble in water with a strong *acid* reaction, it might be an *acid phosphate.* (See the comments following the table.) A *soluble silver* salt cannot be the salt of one of the chloride group of acid ions. The results of the *Preliminary Examination,* especially of 7, p. 92, will also be very helpful.

I. Group of Amphoteric Acids and Related Acids

Ions of Amphoteric Acids: Arseniate, Arsenite, Antimonate, Antimonite, Stannate, Stannite (Platinate, Aurate, Aluminate, Zincate, Plumbite, Chromite).

Ions of Related Acids: Chromate (Dichromate), Permanganate.

45. As a result of the *basic properties* of the *amphoteric acids,* their presence is detected in the *systematic analysis for metal ions.* In a similar way, as a result of the reduction of the chromate-ion (dichromate-ion) and the permanganate-ion by hydrogen sulphide or ammonium sulphide, chromic acid and permanganic acid, if present, would be reduced to chromic-ion and manganous-ion, respectively, and these would be found among the *metal ions.*

In case the metal ion of an amphoteric acid is found in the systematic analysis for metal ions, the corresponding acid ion need not be looked for again in the analysis for acid ions; but the problem must be confronted *whether, in the original substance, the amphoter is present as a basic or an acid component.* For instance, if aluminium-ion is found in the analysis for the aluminium group of metal ions, one must consider whether the original substance contains an aluminium salt or an aluminate.

The decision as to the original rôle of such amphoteric compounds is based on the results of the complete analysis, on the observation of such properties as the neutrality, alkalinity or acidity of aqueous solutions of the original substance, if it is soluble in water, and on the common character of the amphoteric substances; sometimes a decision cannot be reached without the aid of quantitative determinations or of crystallographic examination.

In general, we may note:

1. If the original solution in water is *alkaline*, any amphoteric substance present may be considered *to be present in its acid form* (aluminate, zincate,[1] etc.).

2. If the original solution in water reacts strongly *acid*, and if strong acids are found in the subsequent analysis for acid ions, an amphoteric substance, which may be present, may be considered *to be present in the form of a salt*, or salts, *of its metal ion.* But *arsenic acid* is always present as an *acid* component, its basic properties being so exceedingly slight that no salts of it, as a base,[2] are known. It is soluble in water and the solution reacts decidedly acid.

3. If the original substance is a salt, which is soluble or insoluble in water, and *if no other acid component than the amphoter itself is present* (aluminates, zincates, arsenites, etc.), the amphoter may be considered to form the *acid* component of the salt.

4. If the substance is insoluble in water and other acids are present, crystallographic examination or quantitative determinations of the proportions of bases and acids present would usually be required to determine the rôle, as base or acid, of an amphoter, especially if it is *chiefly base forming.*

46. *Special Indications:*

1. **Arsenic acid,** if found, is always present as the acid or a salt of the acid; it is so strong an acid that salts, in which it forms the basic component, are quite unknown.[2] Arsenic sulphide is precipitated with difficulty, especially in the cold (p. 53, § 2 (*a*)), if

---

[1] If the solution contains free *ammonia*, zinc-ammonium-ion and not the zincate-ion is present.

[2] The pentasulphide, As_2S_5, might be considered a salt, but is chiefly an acid-forming sulphide (see Chapter XIII).

arsenic is present in the form of arsenic acid (difference from arsenious acid). For other differences from arsenious acid, see p. 54, § 3.

2. **Arsenious Acid.** As the name indicates, arsenious acid is more commonly an acid component of a salt than the basic component. But the chloride, bromide, etc., are known, and exist in aqueous solutions, partially hydrolyzed (strong acid reaction). For differences from arsenic acid see 1, above, and see p. 54, § 3.

3. **Antimonic acid** occurs much more frequently as an acid component than as a basic component, **antimonous** hydroxide more commonly as a basic component.

4. **Chromates** and **dichromates** are yellow or red, chromic salts and chromites usually green or violet.[1] This difference in colors between the series of salts enables one to determine, usually, from the color of the original substance, the question whether chromium, when found in the analysis of the aluminium group, is originally present as a **chromate,** a chromium salt or **chromite.** (See also p. 67.) The distinction between chromium salts and chromites is made according to the general rules given in **47.**

5. **Permanganates** are intensely purple, manganous salts pale pink (colorless in solution).

II. The Carbonate Group of Acid Ions

Carbonates, Silicates, Sulphides (Nitrites, Sulphites)

47. The acids of this group, like those of the previous group, should also, generally, be found in the course of the analysis for metal ions, *as a result of the physical separation of carbon dioxide, hydrogen sulphide, silicic acid* (nitrous acid anhydride[2] and sulphur dioxide).

1. **Carbonic Acid.** If a gas is evolved on the addition of an acid to a salt and the gas is without odor, carbonic acid is indicated. Its presence is proved by testing the gas according to p. 69. See there also the test for traces.

2. **Silicic Acid.** The presence of silicates, if present in any but small quantities, is indicated by the *metaphosphate bead test*

---

[1] The color may be modified by the presence of another color producing base or acid (*e.g.* in chrome iron-ore) or of another colored substance.

[2] Its decomposition products, NO and NO_2, are the chief components of the gas. *Cf.* Smith's *General Inorganic Chemistry*, pp. 449, 450.

(5, 1), which should always be made previous to the analysis for metal ions (see p. 87, **1**). Silicic acid is often revealed also by its separation in difficultly soluble form from acid solutions. It may be identified according to p. 69, § 1, or p. 70, § 4. If tin has been found, the test in § 4, p. 70 (SiF_4 test), should be used.

If *silicic acid has not been found* in the course of the analysis for metal ions, a special test for it may be made, according to § 2 (*c*), p. 70, if the substance is soluble in water or acid, and according to § 3, p. 70, if it is insoluble (see also **70,** p. 134). Small quantities of it may otherwise escape detection.

3. **Hydrogen Sulphide.** The presence of sulphides is usually revealed in the preparation of a solution for the analysis for metal ions, by the odor of the acid, when it is liberated from its salts by the action of hydrochloric acid, or, occasionally, by the liberation of sulphur, when the salts are treated with nitric acid or aqua regia.

If hydrogen sulphide has not been found (some sulphides do not liberate H_2S readily, see p. 71, § 1) and there is no reason to conclude that it must be absent (color and solubility of the unknown, taken in connection with the metal ions found), a test for it is made according to p. 71, § 1 or 2, the original substance being used.

4. **Nitrites,** see p. 80. **Sulphites** are decomposed by stronger acids and the odor of sulphur dioxide is perceived. If sulphur is precipitated at the same time, more complex sulphur acids are present (see Fresenius, p. 321).

III. The Preparation of a Solution for Examination for Acid Ions of the Sulphate, Chloride, Phosphate and Organic Acid Groups[1]

48. Two methods of procedure are possible in testing for the **sulphate, chloride, phosphate** and **organic** groups of acid ions: a *nitric acid solution* may be prepared according to **49,** without the removal of metal ions; or, a solution of the *sodium salts* of the acids may be prepared according to **50,** all metal ions, other than the alkali ions, being removed. Each method has its advantages and its disadvantages (see Chapter XVI).

---

[1] The original substance is used for the nitrate group and is also used for some tests in the groups named.

In general, in the absence of substances for which concentrated nitric acid or aqua regia must be used in preparing a solution for the analysis for metal ions, the *nitric acid process* (**49**) is rather simpler and more convenient; in the presence of alkaline earths, aluminium and amphoteric acids, its use is indicated. If an *alkaline* solution (**11**, 3, p. 93) gives a *precipitate* with acids, that requires concentrated nitric acid or aqua regia for solution, the analysis is made more simply by the sodium salt process (**50**, § 3).

The preparation of a *solution of the sodium salts* of the acid ions (**50**) *is to be preferred* when concentrated nitric acid or aqua regia is required to prepare a solution for metal ions, either for the original substance or for a precipitate produced from alkaline solution.

Students should consult their record as to the solubility of the substances and as to the metal ions found and then select the method in **49** or **50**, as indicated.

PREPARATION OF A NITRIC ACID SOLUTION FOR ANALYSIS

49. A solution of the substance, acidified with nitric acid, is prepared, according to the solubility of the original substance, as follows:

1. The *original substance* is *soluble* in *water* with a *neutral* or an *acid* reaction, or it is a *liquid* with a *neutral* or an *acid* reaction. A gram of the substance is dissolved in a little water, 2 to 3 c.c. of dilute nitric acid is added to the solution and the latter diluted with water to 50 c.c.; or, if the substance is a liquid, a measured portion of it (according to its concentration) is diluted to 50 c.c., after it is acidified with 2 to 3 c.c. of nitric acid; or, if the metal analysis showed the liquid to be a *dilute* solution, 50 c.c. of it is acidified with 2 c.c. nitric acid, without further dilution. Analyze the solution according to **51, 52, 54, 55, 57.**

2. The *original substance* is *insoluble* in *water* but *soluble* in *acids.* Warm a gram of the substance gently with 5 to 10 c.c. of dilute nitric acid, dilute the mixture to 50 c.c. with water and heat it to 70° to 80° for a few moments.[1] The solution, or, if a precipitate

---

[1] In the presence of oxidizing agents (chromates, antimonates) *iodide-ion* may be oxidized to iodine. If the color of the solution suggests the presence of any iodine, a little of the solution is tested with chloroform (2 (*a*), p. 73), or with starch solution (4 (*a*), p. 73) for iodine.

remains, the filtrate from the precipitate, is analyzed according to **51, 52, 54, 55, 60,** §§ 2, 4 and 5.

A *precipitate*, insoluble in an excess of acid, may be discarded,[1] except when stannic acid, mercuric-ion, bismuth-ion or lead-ion has been found in the analysis for metal ions.

If *stannic-ion* has been found, the precipitate may contain stannic *phosphate*, which is insoluble in nitric acid; it is reserved for examination according to **54** (see the footnote at that place). *Mercuric, bismuth* and *lead iodides* (and lead bromide) are very difficultly soluble in nitric acid. They are sufficiently soluble[2] in *boiling water* to make the identification of iodide-ion (bromide-ion) possible. If Hg^{++}, Bi^{+++}, or Pb^{++} has been found in the metal ion analysis, the residue, insoluble in nitric acid, may be treated with boiling water and a little nitric acid; the hot liquid is filtered and a portion tested with silver nitrate; if a precipitate forms, the rest of the solution is tested according to **52** (*e*) and (*f*) for iodide-ion (and bromide-ion). While this method reveals the presence of the ions, it does not indicate their quantity; if information on that is desired, the residue is treated by the process given in **50,** 2. According to the instructions given in **48,** this process (**50**) will ordinarily have been used with an unknown containing these salts, as concentrated nitric acid or aqua regia is used in preparing a solution of them for the metal ion analysis.

3. The *original substance* is *soluble* in *water* with an *alkaline reaction* or is a liquid with an *alkaline* reaction. (*a*) Dissolve a gram of a solid substance in as small a volume of warm water as possible, or, if the substance is a liquid, take a portion of it; acidify the solution or liquid with nitric acid, and, if no precipitate is formed, add an excess of 2 to 3 c.c. of nitric acid, dilute the solution to 50 c.c. with water and analyze it according to **51, 52, 54, 55** and **57.**

(*b*) If a *precipitate is formed* when the alkaline solution is acidified with nitric acid, let the precipitate settle, decant the solution from it and try to redissolve the precipitate by warming it with a small excess (3 to 5 c.c.) of dilute nitric acid. The acid solution, whether the precipitate has dissolved or not, is added to the decanted solution, the mixture diluted to 50 c.c., filtered if necessary, and analyzed according to **51, 52, 54, 55** and **57.**

---

[1] If the original substance, or any part of it, was found to be *insoluble in any acid* (p. 98, **18**), the analysis of such an insoluble residue (obtained according to **18**) for *metal and acid ions* still remains to be carried out according to part **E**, p. 130, for "Insoluble Substances," as directed in **18.**

[2] Bismuth and mercuric iodide are hydrolyzed, especially the former.

(*c*) **A precipitate, insoluble in excess of acid,[1] is treated as directed above in § 2.**

PREPARATION OF A SOLUTION OF THE SODIUM SALTS OF ACID IONS

50. If a solution of the sodium salts of acid ions is to be prepared by the removal of metal ions other than the alkali ions, proceed as follows:

1. The substance is *soluble* in *water*, with a *neutral* or *acid* reaction. A gram of the substance is boiled a few minutes with a freshly prepared solution of 2 or 3 grams of sodium carbonate in 10 c.c. of water. The solution is filtered and carefully neutralized with nitric acid. If a precipitate forms when the acid is added, it is best to filter the solution again, before the solution shows an acid reaction. Then a slight *excess* of acid (test) is added, the solution boiled vigorously to remove carbonic acid and diluted to 50 c.c. The solution, which should have a slightly acid reaction, is analyzed according to **51–57.**

Metal ions, other than the alkali metal ions, are precipitated as carbonates and hydroxides by the treatment. Amphoteric hydroxides (*e.g.* aluminium hydroxide, zinc hydroxide, etc.) and some carbonates are somewhat soluble in excess of sodium carbonate and are precipitated by the first addition of acid.

2. The *substance* is *insoluble* in *water* but *soluble* in *acid*.[2] A gram of the substance is fused with 2 to 3 grams of sodium carbonate, the mass formed is extracted with 10 to 20 c.c. of warm water, the extract filtered and treated as described in 1.

Since the alkaline earth phosphates, aluminium phosphate and the alkaline earth fluorides are not readily decomposed by fusion with sodium carbonate, some of the original substance, in nitric acid solution, is tested according to **54** for phosphate-ion, and, in sulphuric acid solution, for fluoride-ion according to **56.**

If a substance containing an organic acid is insoluble in water, it is boiled with sodium carbonate solution, as in §1, *and not fused.*

---

[1] It will be recalled that precipitates from alkaline solutions, which are insoluble in any acid (*e.g.* AgCl, AgBr, $PbSO_4$, etc.), have been reserved (**11,** 3 (*c*), p. 93) for analysis for the metal and the acid ions according to part **E**, p. 130.

[2] If the original substance, or any part of it, was found to be insoluble in any acid (p. 98, **18**), the analysis of such an insoluble residue, reserved in **18,** still remains to be carried out for metal and acid ions according to part **E,** p. 130, for "Insoluble Substances."

3. The *original substance* is *soluble* in *water* with an *alkaline* reaction or it is a liquid with an *alkaline* reaction. A gram of the substance is dissolved in a little water and the solution is carefully neutralized with nitric acid, added drop by drop, or an appropriate portion of the liquid is neutralized with nitric acid.

(*a*) *If no precipitate* is formed when the acid is added, the neutralized solution is analyzed according to **51–57.** If a gas (CO_2, H_2S) is formed, the solution is boiled, before being analyzed.

(*b*) If a *precipitate* is formed, *neutralize* the solution very carefully with dilute nitric acid, added drop by drop, letting the precipitate settle before the addition of a further drop of acid and observing whether the acid produces any further precipitate; or a small excess of the acid is used and the acid solution then neutralized with sodium carbonate (fresh solution). The neutral solution is filtered, rendered slightly acid, boiled to remove carbonic acid and reserved for analysis according to **51–57,** after it has been combined with a solution of the sodium salts of acid ions, *which is obtained from the precipitate* (see (*c*)).

(*c*) The *precipitate*[1] is treated as a new unknown, *i.e.* it is fused with sodium carbonate according to § 2, the mass treated as therein described, and the solution of the sodium salts obtained is combined with that obtained in (*b*). The combined solutions are analyzed according to **51–57.**

Alkaline solutions may give precipitates of *salts* (*e.g.* aluminium phosphate, lead chromate, zinc phosphate, etc.) of amphoteric bases. Ammoniacal solutions, when neutralized, may precipitate salts (*e.g.* cupric phosphate, zinc oxalate) of metal ions which form complex ammonium ions. To remove these metal ions and form sodium salts of the acids, the treatment of such a precipitate is the same as for any salt insoluble in water.

IV. ANALYSIS FOR THE ACID IONS OF THE SULPHATE AND CHLORIDE GROUPS

51. Sulphate-ion. — To a small portion (1 to 2 c.c.) of the nitric acid solution obtained in **49,** 2 or 3 drops of barium nitrate solution are added; or, if the sodium salt solution prepared in **50** is used, a small portion (1 to 2 c.c.) is treated with a drop of dilute nitric acid and 2 or 3 drops of barium nitrate solution. In either case, if *no precipitate* is formed, *sulphate-ion* is absent. If a *precipitate* is formed, a little more of the solution is treated in the same way, the precipitate is allowed to settle, the liquid decanted from it and the residue treated with a drop of dilute nitric acid and 5 c.c. of water. If a precipitate ($BaSO_4$) remains, **sulphate-ion** is present.

---

[1] It will be recalled that precipitates from alkaline solutions, which are insoluble in acid or aqua regia (*e.g.* AgCl, $PbSO_4$, etc.) have been reserved (**11,** 3 (*c*), p. 93) for the analysis for the *metal* and *acid* ions according to **part E.**

If the absence of hydrofluorosilicic acid and fluorides may not be assumed, the precipitate must be further identified as $BaSO_4$, according to § 2, p. 72. $BaSiF_6$, with a drop or two of concentrated H_2SO_4, gives the SiF_4 test, footnote 1, p. 71.

If a sulphide has been found present (**47**, 3), regard must be taken of the fact that hydrogen sulphide is liable to be oxidized to sulphuric acid by prolonged treatment with hot dilute nitric acid or by treatment with concentrated nitric acid. If such treatment has not been avoided, a fresh solution of a little of the original substance is made, hydrochloric acid being used in place of nitric, and the solution is tested as above for the presence of sulphate-ion.

52. The Chloride Group of Acid Ions.—To 1 to 2 c.c. of the nitric acid solution obtained in **49** add a few drops of silver nitrate solution and a few drops excess of nitric acid;[1] or to 1 to 2 c.c. of the sodium salt solution obtained in **50**, add a few drops of nitric acid and a drop or two of silver nitrate solution.[1]

1. If *no precipitate* is formed, the acid ions of the chloride group are *absent*,[2] viz., chloride, bromide, iodide, cyanide,[3] thiocyanide, ferrocyanide, ferricyanide ions. Proceed[4] to **53.**

2. If *silver nitrate* produces a *precipitate* in nitric acid solution, one or more of the acid ions mentioned in 1 must be *present*. If

---

[1] If sulphides have been found according to **47**, 3, the acid solution is first warmed until the hydrogen sulphide is expelled; a *black* precipitate with $AgNO_3$ would indicate that it had not all been removed.

[2] It will be recalled that *insoluble salts* of these ions (*e.g.* AgCl, AgBr, etc.) are analyzed according to part E, p. 130.

[3] If *mercuric-ion* has been found, a special test for cyanide-ion must be made after Hg^{++} has been removed by H_2S (see § 4, p. 76).

[4] If the solution tested contains no metal ions other than the alkali metal ions, a few drops of dilute ammonium hydroxide are allowed to flow down the side of the test tube and form a layer over the solution to which nitric acid and silver nitrate have been added. At the *neutral point*, a yellow precipitate would indicate silver phosphate or arsenite; a red-brown precipitate indicates silver arseniate or chromate; a white precipitate, silver borate, oxalate, silicate or carbonate.

a silver salt is precipitated, note its *color*, and then test for the acid ions in the following order, in small portions (1 to 2 c.c.) of the nitric acid solution prepared according to **49**, or of the sodium salt solution prepared according to **50.**

(*a*) **Thiocyanide-ion** (white silver salt). — Test the solution with $FeCl_3$ and ether (p. 28, § 4 (*c*) and p. 76).

(*b*) **Ferrocyanide-ion** (white silver salt). — Test the solution with $FeCl_3$ (pp. 28 and 76).

(*c*) **Ferricyanide-ion** (red-brown silver salt).— Test the solution with ferrous ammonium sulphate (fresh solution) (pp. 32 and 76).

(*d*) **Cyanide-ion** (white silver salt). — Test the solution with $FeSO_4$ and $FeCl_3$, according to 2, p. 76, or test the solution according to 3, p. 76. If mercuric-ion is present, it must be removed by means of H_2S, before these tests are made (see 4, p. 76).

(For the detection of cyanide-ion in the presence of sulphides consult Fresenius, p. 376.)

(*e*) **Iodide-ion** (yellow silver salt). — Test the solution with sodium nitrite and starch (4 (*a*), p. 73) or with chlorine water and chloroform (2 (*a*), p. 73, and 4 (*b*), p. 74). In the presence of cyanide-ion use the process described in (*g*) below.

(*f*) **Bromide-ion** (pale yellow silver salt). — Test the solution with chlorine water and chloroform (2 (*a*), p. 73, 4 (*b*), p. 74). In the presence of iodide-ion, test for bromide-ion according to 4 (*b*) or 5, p. 74. In the presence of cyanide-ion, proceed according to the process described in the next paragraph (*g*).

(*g*) **Chloride-ion** (white silver salt). — In the absence of cyanide, sulpho- and ferrocyanide ions, a white silver salt, insoluble in nitric acid, shows the presence of **chloride-ion.** In the presence of bromides or iodides, test for *chlorides* according to p. 74, 4 (*c*) or 5. In the presence of cyanides, precipitate the silver salts, in 5 c.c. of the solution, by an *excess* (test) of silver nitrate and collect the salts on a filter. The dry silver salts are fused in a porcelain crucible, to decompose the cyanide (hood!), and the residue is fused again, after the addition of sodium carbonate. The aqueous extract of the cooled mass is acidified with nitric acid and then tested for the halogens according to p. 74, 4 or 5.

N.B. Sulpho-, ferro- and ferricyanides also interfere with the tests for iodides, bromides and chlorides. If these ions are present, proceed according to Fresenius, p. 376.

V. ANALYSIS FOR THE PHOSPHATE GROUP OF ACID IONS

The group tests in **53** are to be carried out only if all metal ions other than those of the alkali group are absent. The solution of sodium salts, prepared according to **50,** may be used for the group tests; but the nitric acid solution, prepared according to **49,** may be used for the group tests, only *if the original substance consisted wholly of alkali salts or free acids.* A nitric acid solution prepared according to **49,** and containing metal ions other than the alkali ions, is examined *directly* according to **54** to **57** for *phosphate, borate, fluoride* and *oxalate* ions.

53. *Metal ions other than those of the alkali metals are absent.* 2 or 3 c.c. of the solution[1] are treated with 4 or 5 drops of *calcium* chloride solution and neutralized with a drop or two of ammonium hydroxide solution.

1. The *absence* of a *precipitate* proves the absence of phosphate, fluoride and oxalate ions, and of notable quantities of borate ions, *in the solution.* If the original substance does not contain alkaline earths or aluminium, the tests for phosphate-ion (**54**) and fluoride-ion (**56**) may be omitted; but if the original substance does contain the earths or aluminium, *the tests must be made* in *spite of the negative result of the group test* (see **50,** 2). Small quantities of borates must also be looked for according to **55.**

2. A *precipitate* shows that one or more of the acids of this group *may be present;* but silicate, arsenite, arseniate, tartrate (and sulphate) ions also form precipitates under the same conditions. If these have been excluded by the previous history of the analysis (**1, 46, 47, 51**), the precipitate must represent a calcium salt of an acid of the phosphate group. However this may be, the mixture, holding the calcium salt as a precipitate in suspension, is next rendered acid with *acetic acid.*

(*a*) A white precipitate, insoluble in acetic acid, would indicate the *presence* of *fluoride* or *oxalate* ions.[2] Calcium fluoride is a gelatinous, calcium oxalate a white crystalline precipitate. If such a precipitate remains, the substance is tested for fluoride and oxalate ions according to **56** and **60**, 2, and also for phosphate and borate ions, according to **54** and **55**, since a partial solution (not always noticeable) of the calcium salt precipitate may have taken place.

---

[1] The solution must be free from carbonate. If carbonic acid has not previously been expelled (in **50**), the solution is acidified with hydrochloric acid, until all the carbonate is destroyed, and the solution boiled to remove all the carbon dioxide.

[2] Silicic acid, if present in quantity, may also separate out.

(*b*) If the precipitate dissolved completely in acetic acid, tests for phosphate and borate ions are made according to **54** and **55**, and the tests for fluoride and oxalate ions are omitted.

54. Phosphate-ion. — Use the nitric acid[1] solution prepared according to **49**, or the solution of sodium salts prepared according to **50**, or a solution of 0.1 gram of the substance in 1 to 2 c.c. of nitric acid[1] and sufficient water to make about 5 c.c. of solution.

1. Add 1 c.c. of the solution to 10 c.c. of ammonium molybdate solution (*nitric acid solution*[2]). If no precipitate forms in the course of a minute, add 4 c.c. more of the solution of the substance and allow the mixture to stand at room temperature. A *yellow precipitate* of ammonium phosphomolybdate shows the presence of **phosphate-ion.** The precipitate may be examined further according to § 3 (*b*), p. 78.

Arsenic acid does not produce a precipitate with molybdate solution at ordinary temperatures; it does when the mixture is heated. If arsenic has been found, the test for phosphoric acid may be carried out in the cold, and the phosphate confirmed according to the method given, or the arsenic may first be removed by precipitation, at 70° to 80°, with hydrogen sulphide.

Iodides are likely to interfere with the action by reducing molybdic acid and forming free iodine. If iodides are present in more than small quantities, and if a green mixture is formed when the test with molybdic acid is tried, the iodide-ion must be removed. The nitric acid solution is evaporated to dryness, the residue treated with 1 or 2 c.c. of concentrated nitric acid and the acid evaporated. The residue is dissolved in a little dilute nitric acid and water and tested as described above. The iodide-ion may also be removed by means of silver nitrate. As large quantities of *chlorides* render the reaction somewhat less sensitive, for the most exact work chloride-ion may be removed either by silver nitrate or by evaporation with nitric acid, as described for the iodide-ion.

---

[1] *Stannic phosphate* is insoluble in nitric acid. If *tin* has been found, it is removed, by precipitation with hydrogen sulphide in hydrochloric acid solution; the filtrate is evaporated to dryness and a nitric acid solution of the residue tested as above.

[2] If an ammonium molybdate solution *without nitric acid* is used (see table of reagents, p. 144), 5 c.c. of the molybdate solution is mixed with 5 c.c. of nitric acid before the reagent is ready for use. The addition of ammonium nitrate (about 1 gram to 10 c.c.) increases the sensitiveness of the solution.

2. *In the absence of metal ions other than the alkali ions*, the tests with magnesium mixture and with silver nitrate, given in § 2, p. 78, may be used.

55. Borates. — Some of the solution prepared in **50**, or of the solution prepared in **49**, or of the original substance, is tested according to one of the following methods:

1. The *turmeric paper test*, § 2, p. 79.

Ferric salts, chromates, chlorates and iodides interfere with the test. In the presence of any of these substances, one of the tests that follow may be tried; or ferric-ion may be removed by sodium carbonate, chlorates destroyed by ignition of the salts, chromates reduced in dilute acid solution by H_2S, iodide-ion removed by $AgNO_3$, and the excess of silver-ion, used, by KCl.

2. The *(alcohol) flame test*, § 3, p. 79.

Copper, if present, is removed by H_2S. The halide ions, if present in more than traces, may lead to the formation of a green-edged flame of ethyl halide (*e.g.* C_2H_5Cl); if they are present, they are most conveniently removed by means of a concentrated solution of silver nitrate, before the test is made.

3. The *fluoride flame test*, described in § 4, p. 79.

The test is a very sensitive one, but the spectroscope should be used to identify the flame. Organic fluorides, formed in the flame, barium, manganese and copper give green flames which must not be mistaken for a boron flame.

56. Fluoride-ion. — The tests given in § 2 or 3, p. 77, may be used with a *portion* of the unknown. They are carried out in (sulphuric) acid mixtures.

57. Oxalate-ion. — See below, **60**, 2 (*a*) or (*b*).

VI. Analysis for the Nitrate Group of Acid Ions

58. Chlorate-ion. — A small portion of the original unknown is tested according to § 1, 2 or 3, p. 80.

59. Nitrate-ion. — A small portion of the original substance is tested according to § 2, p. 80. See § 4, p. 80, in regard to the precautions required when *nitrites* are present.

If chlorates, chromates, iodides or bromides are present, use the test given in § 3, p. 80, removing any ammonia, that may be present, by boiling the alkaline solution before zinc and iron are added.

VII. Analysis for Organic Acid Ions[1]

60. Organic acids should only be looked for if their presence is indicated by the preliminary tests in **2** or **7,** pp. 89, 90 and 92. In doubtful cases, the test given on p. 81 may be used as well.

1. **Acetate-ion.** — Test the unknown directly according to § 2 or 3, p. 82.

2. **Oxalate-ion.** — (*a*) Treat a small amount of the unknown, or of the nitric acid solution prepared in **49,** or of the sodium salt solution prepared in **50,** with warm dilute sulphuric acid (if a carbonate is present, the carbon dioxide is removed by boiling); cool the solution, and add manganese dioxide (free from carbonate) to it, irrespective of the presence of any precipitate: effervescence of carbon dioxide (limewater test) proves[2] the presence of **oxalates.**

(*b*) If the unknown is soluble in water (or acetic acid), or if the acids of the unknown are converted into sodium salts by the method described in **50,** add calcium chloride and acetic acid, in excess, to the aqueous solution. A precipitate would be calcium **oxalate** or calcium fluoride; the former is a white, crystalline, pulverulent precipitate, the latter an opalescent, semitransparent precipitate. In case of doubt, the precipitate is collected and tested according to (*a*) with manganese dioxide in dilute sulphuric acid solution.

3. **Tartrate-ion.** — To test for *tartrates,* all metals, except the alkalies, should be removed, as far as possible (see, however, **33,** 1, in regard to aluminium and chromium). About one-half gram of an unknown solid, or the proportionate amount of an unknown solution, is freed from the heavier metal ions by means of hydrogen sulphide, ammonium sulphide and ammonium or sodium carbonate. The filtrate from the last precipitate obtained is rendered acid with hydrochloric acid and concentrated to a small bulk (10 c.c.), carbonic acid being removed by the same operation. The solution is then tested for tartrates according to § 3

---

[1] Only the acids on pp. 82 to 86 are considered. For tests for the innumerable other organic acids, Fresenius, Mulliken's "Identification of Organic Compounds" and similar works should be consulted.

[2] If organic acids other than those described here must be considered, (*a*) and (*b*) should both be used to identify oxalate-ion. Formates, for instance, give the test described in (*a*), although less vigorously.

(*a*), (*b*) and (*c*) p. 83; it must respond to all three tests if **tartrates** are present.

4. **Benzoate-ion.** — From a rather concentrated solution of a benzoate, **benzoic acid** may be precipitated by acid. It is identified by its melting point (§ 1 (*a*), p. 84), and by the ferric chloride test (§ 2, p. 85). Dilute solutions (*e.g.* food preparations) are treated as follows: The solution is acidified with sulphuric acid and shaken, in a separatory funnel,[1] with sufficient ether to form a distinct layer containing 20 to 30 c.c. of ether. The ether layer is separated, filtered through a small filter moistened with ether, and the ether allowed to evaporate spontaneously. Crystals, remaining, may be tested by their melting point and by the ferric chloride test (pp. 84–5). Careful sublimation of the acid in an inclined test tube, or between a pair of watch crystals, may be used to purify the acid, if necessary.

For the ferric chloride test the residue, left by the evaporation of the ether extract, is dissolved in a few drops of ammonium hydroxide solution, the solution is warmed on a steam-bath until it is neutral to litmus, and filtered, through a very small filter, into a narrow test tube. The filtrate is tested with a drop of neutral ferric chloride solution.[2] A flesh-colored precipitate shows the presence of a **benzoate**.

5. **Salicylate-ion.** — The method of testing described for benzoic acid is used and salicylic acid identified by its ferric chloride reaction or its melting point (p. 86); the process described under benzoic acid, p. 84, § 1 (*a*), is used. Salicylic acid in dilute solution (*e.g.* food products) may be found by the same process as given for benzoic acid and the tests for the two acids are made simultaneously. Instead of ether, chloroform may be used and the chloroform extract tested directly for salicylic acid by covering it with a dilute solution of ferric chloride.[3]

E. THE ANALYSIS OF SUBSTANCES INSOLUBLE IN WATER, ACIDS AND AQUA REGIA. THE ANALYSIS OF SILICATES.

61. The most common and widely occurring insoluble substances are *silicates* and *silicon dioxide*. Related to these are

---

[1] A bottle, preferably with flat sides, may be used in place of a separatory funnel, and the ether layer carefully decanted over the shoulder of the bottle.

[2] Leech, *Food Inspection and Analysis*, 1909, p. 828.

[3] Peters, Bull. 65, p. 160, U. S. Department of Agriculture.

stannic oxide, aluminium oxide (native or ignited) and *aluminates, chromic oxide* (ignited) and *ferrous chromite* (chrome iron ore). There is also an insoluble modification of *chromium chloride* and one of *chromium sulphate*. The *sulphates* of *barium, strontium* and *calcium, calcium fluoride* (and other fluorides) are of rather common occurrence. Certain silver and lead salts, viz., *silver chloride, bromide, iodide* and *cyanide*, and *lead sulphate*, a number of ferro- and ferricyanides, etc., and *carbon* and *sulphur* complete the list of substances we are most liable to meet in this division. Although the lead and silver salts and fluorides are of less common occurrence than many of the other substances mentioned, the methods of analysis make it advisable to *remove* lead and silver salts, if they are present, and to have warning of the presence of fluorides, if they are present, before proceeding to the more common cases. The method of analysis given below is based on this idea. However, careful inspection of the substance and the application of the few preliminary tests given, if not made previously, will, as a rule, enable one to shorten the scheme of analysis greatly and to go directly to the paragraphs whose instructions must be followed in a given case.

I. Preliminary Examination

62. Examine the substance carefully. **Carbon** (graphite, coal, etc.) and **sulphur** will usually reveal themselves by their color, **quartz** often by its appearance. **Carbon** may be confirmed by burning some of the substance on a platinum foil, or on a porcelain crucible lid, heated to bright redness. **Sulphur** may be confirmed by heating some of the substance in a small tube — a sublimate of sulphur will form — and by burning some on a porcelain crucible lid.

63. Heat some of the pulverized substance with sodium carbonate in the reducing flame of the blowpipe[1] (see **3,** p. 90). Metallic beads will indicate the presence of **lead, silver** or **tin.** The presence of any or all of them can be most readily determined by analysis of the beads: the metal or alloy is treated according to II, **19,** p. 98, and analyzed for the metals mentioned.

If *lead* is found, proceed, after completing the preliminary tests, with the *analysis* of the substance itself according to **67**, below, *otherwise omit that section;* if *silver* is found, proceed similarly to **68**, *otherwise omit it.* If both have been found, proceed first to **67** and then to **68**. The further course, if *tin* is found, depends on the results of the remaining preliminary tests.

---

[1] The addition of a little potassium cyanide makes the reduction easier.

64. A small portion of the original unknown is tested with the metaphosphate bead (p. 91, **5**, (1)) for **silicic acid**; another portion is fused in the loop of a platinum wire with sodium carbonate. Effervescence indicates silicic acid. If *tin* has been found *absent* (**63**), and if the metaphosphate and sodium carbonate beads show the presence of a silicate, proceed to **69**, p. 134, and make a test for fluorides, and then *proceed to* **70–73**, *and make a silicate analysis.* If tin has been found present, in **63**, test the substance for silicic acid by the SiF_4 test (§ 4, p. 70), and if its presence is confirmed, proceed as just stated.

In the absence of silicic acid, proceed to **69** and **74**, omitting **70–73**.

65. Heat some of the substance, on a platinum wire, in the reducing zone of the flame of the bunsen burner, cool it in the inside cone of the flame and then moisten the residue with a drop of hydrochloric acid. Hydrogen sulphide (p. 72, § 2) indicates a **sulphate**, and the chlorides formed, heated in the edge of the flame, will reveal **calcium, strontium** and **barium**, if present — often all three in succession, if they are all present. The rigorous analysis is made according to **74**, p. 138.

66. Test the substance for complex cyanides according to p. 89, **2**, (1) (*f*) and (*h*). If such are found to be present, proceed according to Fresenius, p. 529.

II. Analysis

67. Examination and Removal of Lead Salts. — If lead has been found or indicated in the preliminary test **63**, heat about a gram[1] of the substance with a concentrated, slightly acid solution of ammonium acetate[2] until all the lead (excepting lead silicate, if it is present) has been dissolved (test, see § 1, below); reserve an insoluble residue for analysis according to **68–74** and test the solution as follows:

---

[1] If this quantity is not available, less is used and proportionately smaller quantities used for the tests: good results can, with care, be obtained even with *drop* tests.

[2] The solution is prepared by dissolving ammonium acetate in its own weight of water. It is tested with sensitive litmus, and if it does not redden it, acetic

1. For **lead:** dilute a portion of the solution with about 10 volumes of water and add potassium chromate to the diluted solution: a yellow precipitate is confirmed as $PbCrO_4$ according to § 2 (*c*), p. 44. A second portion of the solution is tested with H_2S, if the chromate test proved negative. A black precipitate is collected, dissolved in a little dilute nitric acid, the solution is evaporated and the residue tested with potassium chromate (§ 2 (*c*), p. 44).

2. For **sulphate-ion:** barium chloride and hydrochloric acid are added to a small portion of the solution, diluted with about 10 volumes of water.

3. For **chloride-ion:** dilute a portion with 20 volumes of water (to avoid the precipitation of silver acetate) and add silver nitrate and nitric acid to the solution. If a precipitate is formed, allow it to subside, decant the liquid and digest the precipitate first with water and a drop or two of nitric acid, and then with ammonia solution. Filter the solution, if necessary, and acidify the filtrate with nitric acid; a precipitate is silver **chloride.**

68. Examination and Removal of Silver Salts. — If silver has been found or indicated in the preliminary test **63,** a portion of the unknown which has been freed from lead according to the preceding section **67,** or which has been found free from it, is used.

1. It is warmed with a little potassium cyanide solution. Any undissolved part is reserved for analysis according to **69–74.** The solution is filtered, diluted and acidified with dilute nitric acid. (Care! hood! hydrocyanic acid fumes!) A precipitate **P** is collected, washed well, reduced on charcoal, or by ignition with sodium carbonate in a porcelain crucible, and a metallic product tested for **silver.** The filtrate from the precipitate **P** is tested for **sulphates** by barium chloride.[1]

2. The determination of the **acid ions,** combined with silver in the original substance, is based on the following considerations:

---

acid is added to it, until slight acidity is indicated. If in doubt as to the presence of lead salts, extract the substance first with only 2 or 3 c.c. of the solution and test the solution thus obtained.

[1] See Fresenius, p. 524, second footnote.

(*a*) If the substance under examination is the original substance, or a residue left after the substance has been extracted with water and with dilute hydrochloric acid or nitric acid (**14, 15, 16**), or with ammonium acetate (**67**), the determination of the acid ions may be made directly, according to (*b*), with the substance under examination. But if the substance under examination is a residue left after treatment of the original substance with *aqua regia*, account must be taken of the fact that aqua regia converts silver bromide, iodide and cyanide into silver chloride. In such a case, to determine the possible presence of Cl^-, Br^-, I^- and CN^- in the original material, a small amount of the latter (0.25 gram) is extracted with water and dilute nitric acid; the residue **R** is treated according to (*b*).

(*b*) The substance, or the residue **R,** obtained in (*a*), is treated with a piece of zinc and dilute sulphuric acid. When the silver salt is reduced, the acid solution is decanted and a portion tested for **cyanide-ion** according to p. 76, 2 (*a*). In the absence of cyanides the rest of the solution is tested according to p. 125, **52,** 2 (*e*, *f*, *g*), for **iodide, bromide** and **chloride** ions. If cyanide-ion is found, the process described in **52,** 2 (*g*), p. 125, is used for the detection of the halide ions mentioned.

69. Examination for Fluorides. — Make the following tests with small portions of the substance freed from lead and silver (**67, 68**), or of the original substance, if lead and silver are absent.

1. Make a test with concentrated sulphuric acid and silica according to § 3, p. 77, or try the etching test in § 2, p. 77.

2. If the test has given negative results, fuse some of the substance with 4 to 6 parts of sodium carbonate on some platinum foil. The fused mass is extracted with 5 to 10 c.c. of warm water, the liquid filtered and concentrated to 2 to 5 c.c. The solution is acidified with acetic acid, filtered if necessary, and treated with calcium chloride (§ 1, p. 76). If a precipitate is formed, it is collected on a small filter, dried and tested for fluoride by one of the two methods given in 1 above (preferably by the SiF_4 test, § 3, p. 77).

Some fluorides (*e.g.* fluorspar) are scarcely decomposed by sodium carbonate, others (in silicates) are not decomposed by sulphuric acid.

70. The Analysis of Silicates. — The presence of a silicate is indicated by the preliminary examination **5** (1), p. 91, or by that in **64,** p. 132.

A little of the silicate is tested to see if it can be decomposed by acids, the finely pulverized substance being heated with nitric acid; the formation of a gelatinous or flocculent precipitate would indicate that the silicate is *decomposable* by acid. If it is completely decomposed by acid, proceed according to **71,** otherwise proceed to **72.** An alkaline *liquid* containing a silicate is treated according to **71.**

A test for fluorides, according to **69,** *should have been made before the silicate analysis is started. If fluorides are present, the analysis of silicates must be carried out in platinum vessels.*

71. Silicates which are Decomposed by Hydrochloric or Nitric Acid. — 1. Heat a gram of the finely pulverized substance with 20 c.c. of nitric acid[1] in a porcelain dish on the steam bath. Stirring and the breaking up of lumps of gelatinous silicic acid promote the decomposition. When all gritty particles have disappeared, the silicate may be considered to be completely decomposed. One-third of the mixture is reserved for the examination for acid ions according to § 3, below; the rest of it, without filtration, is evaporated to dryness on the steam bath, the residue moistened with concentrated nitric acid, and the latter evaporated. The residue is dried 15 minutes at 120°, heated with 4 to 5 c.c. of dilute nitric acid, and 50 to 60 c.c. of water are subsequently added. The solution is filtered and the *filtrate* used for the analysis for all the metal ions according to part **C**, p. 100.

2. The *residue*, insoluble in nitric acid, may contain, besides **silicic acid,** (meta)stannic acid, antimonic acid, and bases or acids combined with them. It is heated with 1 c.c. of concentrated hydrochloric acid[2] in a test tube, the acid is decanted, diluted with water to 50 c.c. and saturated with hydrogen sulphide in the cold. The absence of a colored precipitate shows the absence of stannic acid and other metal oxides in the residue. The presence of **silicic acid** is confirmed by the SiF_4 test, § 4, p. 70.

If the hydrogen sulphide test indicated the presence of stannic acid or other metal oxides in the residue, the latter is heated for 30 minutes with 10 c.c. of concentrated hydrochloric acid,[2] the acid decanted and the extraction repeated. The residue is tested for **silicic acid** according to § 4, p. 70. The hydrochloric acid extract is evaporated, but not quite to dryness, and the residue dissolved in water, with the aid of some warm dilute hydrochloric acid if necessary. The acid solution is analyzed according to **21, 22,** etc. (p. 100), *for the copper and arsenic groups.* The filtrate from the copper and arsenic groups is tested for *phosphoric acid* according to **54.**

---

[1] Nitric acid is to be preferred to hydrochloric acid to avoid separate treatment for arsenious acid, whose chloride is volatile.

[2] *Cf.* Noyes and Bray, *J. Am. Chem. Soc.*, **29,** 154 (1907).

3. *Examination for Acids other than Silicic Acid (and the Amphoteric Acids).* — (*a*) **Amphoteric** and related acids (see p. 116) are found in the analysis for metal ions.

(*b*) **Carbonates** and **sulphides** will usually reveal themselves in the process of solution of the silicate. Any gas evolved is examined according to **47,** p. 118. A special test for sulphides, if considered desirable, may also be made as directed in **47,** 3, p. 119.

The portion of the nitric acid solution reserved in **71,** 1, for the examination for acid ions, is filtered and tested as follows:

(*c*) Silver nitrate is added to a small portion (1 c.c.) of the solution. A *precipitate* indicates the presence of the **chloride** group of acid ions; further tests are made according to **52,** p. 124.

(*d*) Barium nitrate is added to another small portion to test for **sulphate-ion.** A precipitate is confirmed as barium sulphate according to **51.**

(*e*) Another portion is examined for **boric acid** according to **55,** 1 or 2.

(*f*) A further portion is evaporated to dryness on the steam bath, the residue is heated on the steam bath for an hour and then extracted with dilute nitric acid and tested for **phosphoric acid** according to **54.** (In the presence of *stannic acid,* phosphoric acid is found as described above in § 2.)

(*g*) A test for **fluorides** should have been made with the original substance according to **69,** p. 134. A test for **nitrates** (*e.g.* in water glass) is made with the original substance according to **59.**

72. Silicates which are not Decomposed by Hydrochloric or Nitric Acid. — Such silicates would appear as "insoluble substances." Lead[1] and silver salts, if present in the original substance, should be removed according to **67** and **68;** sulphur, if found (**61**), is removed by ignition of the substance in a porcelain crucible. A test for fluorides (see **70** and **69**) should precede the silicate analysis. About one gram of the finely pulverized silicate is mixed with two parts each of sodium and potassium carbonates[1] and with a little potassium nitrate, and the mixture fused in a platinum dish. (Consult the instructor. Read the precautions in Fresenius, pp. 20–21, in regard to the proper use of platinum vessels.) The cooled mass is digested with a little warm water and decomposed by nitric acid, used in excess. The further treatment and examination for metal ions and for acid ions is then carried out as in **71**, except that **74**, 1 to 7, is substituted for **71**, 2 (examination of the silicic acid residue), and *a special examination* for alkalies is made according to **73**.

---

[1] Lead, in the form of lead silicate, cannot be removed by the process given in 67 and is still present, if contained in the substance.

73. Analysis for Alkalies in Silicates that are not Decomposed by Acids. — One of the following three methods may be used. Method 1 is the most rapid and convenient, but gives little information as to the quantities of the alkali metals present. If such information is desired, method 2 or 3 should be used.

1. A little of the pulverized silicate is mixed with ammonium fluoride and the mixture gently heated, in the bunsen flame, on the loop of a platinum wire. The mass is then extracted with a drop of water, and the flame test made for the **alkalies**, with the aid of the spectroscope (see p. 5, 7 (*c*)).

2. About half a gram of the pulverized silicate is heated in a platinum dish (Instructor) with a little water and with 5 c.c. each of hydrochloric and hydrofluoric acids. (Care! Work in a hood. The vapors injure the lungs and the skin!) When the silicate has dissolved, 5 c.c. of dilute sulphuric acid is added, and the contents of the dish evaporated in the hood, until heavy fumes of sulphuric acid are formed. The cooled residue is extracted with water, all the metals, excepting the alkalies, are removed by the group reagents, and the alkalies tested for according to **43**, p. 114.

3. The finely pulverized silicate is mixed with one part of pulverized ammonium chloride and eight parts of pure calcium carbonate, and the mixture heated in a covered platinum crucible, to a moderate red heat, for half an hour. The cooled mass is extracted with water, ammonium carbonate and ammonium hydroxide are

---

[1] The mixture melts lower than either carbonate alone.

added to the filtered extract, and the filtrate from the precipitate, which is produced, is examined according to **43,** p. 114.

74. Examination for the Remaining Substances Enumerated in 61. — 1. Silver and lead being absent or having been removed by ammonium acetate and potassium cyanide, according to **67** and **68**, the substance is mixed with two parts each of sodium and potassium carbonates and a small amount of potassium nitrate, and the mixture fused in a small platinum dish. (Consult the instructor. Read Fresenius, pp. 20, 21, in regard to the proper use of platinum ware.) The cooled mass is warmed with 50 c.c. of water, the solution is filtered and the filtrate **F** analyzed according to §§ 2 to 6. The residue **R** is washed with more water, and analyzed according to § 7 for metal ions.

2. Acidify about 25 c.c. of the filtrate **F** with hydrochloric acid, evaporate the solution to dryness, and dry the residue for one hour on the steam bath, or for ten minutes in an air bath at 120°, to render any silicic acid insoluble. Heat the residue with water and hydrochloric acid. An insoluble residue would be **silicic acid** (see p. 70, § 4, for a confirmatory test). If a large amount of silicic acid is found, the substance is a silicate and the analysis should be continued according to **72–71.** A small amount of silicic acid, which very frequently is found in minerals and ores, is removed by filtration, and the solution **S** is tested according to § 3 (below) for *lead,*[1] *tin, aluminium, chromium* and *zinc.* (Why are these the only common metal ions, besides the alkalies, which can be present in this solution? In the form of what compounds are they obtained by the fusion with alkali carbonates? If found, does their presence at this place prove anything as to their occurrence in the original substance as basic or acid constituents?)

3. (*a*) Saturate the solution **S,** obtained in 2, with hydrogen sulphide. *If no precipitate is formed,* proceed to (*c*). A *precipitate* is collected and the *filtrate* examined according to (*c*). The precipitate is extracted with ammonium sulphide; a black residue indicates **lead,** which is confirmed according to **67,** 1. Examine the ammonium sulphide extract according to (*b*).

(*b*) Acidify the ammonium sulphide extract, obtained in (*a*); a yellow precipitate is collected and treated with hot concentrated hydrochloric acid and the solution, resulting, is tested for tin according to § 2 (*b*), p. 57.

---

[1] Lead is usually found and removed according to the method described in **67,** but, in the form of lead silicate, it may escape detection by that method.

(*c*) After removing any tin or lead, if present, by hydrogen sulphide (see *a*), add ammonia and ammonium sulphide to the solution. Collect a precipitate, dissolve it in hydrochloric acid and boil the solution, obtained, to remove hydrogen sulphide. Then add ammonium hydroxide to it, until it reacts slightly alkaline. A precipitate is collected and tested, according to IV, § 1 or 2, p. 38, for **aluminium-ion** and **chromium-ion** (for the latter only if a chromate has been reduced by hydrogen sulphide in the removal of lead or tin). The filtrate from any precipitate formed by ammonium hydroxide, or the solution in which this failed to give a precipitate, is tested for **zinc-ion** according to p. 40, § 2 (*b*).

4. Another portion of the filtrate **F,** obtained in 1, is acidified with hydrochloric acid and tested:

(*a*) With barium chloride for **sulphate-ion.**

(*b*) With hydrogen sulphide, passed into the hot solution, for **arseniate-ion.** A precipitate is tested for **arsenic** by means of potassium cyanide (p. 55, § 4 *b*).

Owing to the use of an oxidizing agent, potassium nitrate, in the fusion, the form of the arsenic, if found, in the original unknown must be ascertained according to the considerations discussed in **45.**

5. Another small portion of **F** is acidified with *nitric acid,* and a part tested, in the cold, with molybdate solution for **phosphate-ion** (p. 78, § 3), and a second part with silver nitrate for the **chloride group** of acid ions. If a precipitate is formed, further portions are tested according to **52** for the members of the group.

6. If the filtrate **F** is yellow, confirm the presence of **chromate-ion** by means of lead acetate and acetic acid. (Does the presence of chromate-ion here enable us to decide whether chromium was originally present with a valence of three or six? See **46,** 4.)

7. The residue **R,** obtained in **74,** 1, contains the *metal ions,* present in the insoluble unknown, in the form of carbonates or oxides, excepting possibly the ions of bases which, owing to the amphoteric character of the metal hydroxides, were found, in part, at least, in **74,** 3. The residue **R** is dissolved in dilute nitric acid, and the acid solution analyzed according to the systematic method of analysis, Part **C,** p. 100.

APPENDIX

TABLE OF SOLUBILITIES

SOLUBILITIES.[1][2]

		Hydrogen.	Sodium.	Potassium.	Ammonium.	Magnesium.	Calcium.	Strontium.	Barium.	Aluminium.	Chromium.	Ferric.	Ferrous.
1	Oxide...........	....	w	w	....	A	W-A	W	W	A&I_9	A & I_{10}	A	A
2	Hydroxide......	....	W	W	W	A	W-A	W	W	A	A	A	A
3	Chloride........	W	W	W	W	W	W	W	W	W	W & I_{11}	W	W
4	Bromide........	W	W	W	W	W	W	W	W	w	W & I	W	W
5	Iodide..........	W	W	W	W	W	W	W	W	w	w	w	W
6	Cyanide.........	W	W	W	w	w	W	W	W-A	......	a	....	a-i
7	Ferrocyanide....	w	W	W	w	w	w	W	w-a	i	....	I	I
8	Ferricyanide	w	W	W	w	w	w	w	w	......	....	w	I
9	Sulphocyanide...	w	W	W	W	w	w	W	w	W	w	w	w
10	Sulphide........	W	W	W	W	a_4	W-A_6	W	W	a	a-i	a	A
11	Sulphate........	W	W	W	W	W	W-I	I	I	W	W & I	W	W
12	Carbonate.......	W_1	W	W	W	A	A_7	A	A	......	a*	a*	A
13	Arsenite.........	....	W	W	w	a	a	a	a	......	....	a	a
14	Arseniate........	w	W	W	w	a	a	a	a	a	a	a	a
15	Chromate.......	w	W	W	w	w	W-A	W-A	A	......	a	w	....
16	Phosphate.......	W	W	W	W	A_5	A_8	A	A	A	a	A	A
17	Borate..........	W	W	W	w	w-a	a	a	a	a	a	a	a
18	Fluoride.........	W	W	W	W	a-i	A-I	A-I	A-I	w	w	w	w-a
19	Silicate..........	I_2	W	W	....	a	a	a	a	A-I	a	a	a
20	Nitrate..........	W	W	W	W	W	W	W	w	W	W	W	W
21	Chlorate........	w	W	W	W	w	w	W	w	w	w	w	....
22	Acetate.........	W	W	W	W	W	W	W	W	W	w	W	W
23	Oxalate.........	W	W	W	W	a	A	a	a	a	w-a	a	a
24	Tartrate.........	W	W	W_3	W_3	w-a	a	a	a	w	w	W	w-a

[1] *W* Soluble in water.
A Soluble in acid (hydrochloric or nitric acid or aqua regia).
W-A Somewhat soluble in water, soluble in acids.
W-I Somewhat soluble in water, scarcely more soluble in acids.
A-I Difficultly soluble in acids.
I Insoluble in water and acids.
Small letters are used for less common salts.

[2] See the *comments* **following.** The *sub-indices* refer to the *numbered comments.*

* Basic salts.

COMMENTS ON SOLUBILITIES

It should be remembered that salts, insoluble in water, often *appear* to be rendered soluble, by forming new salts, of *complex ions*, with other salts; for instance, silver cyanide is insoluble in water, but forms with potassium cyanide a soluble salt, K[Ag(CN)$_2$], (p. 43); mercuric iodide is insoluble in water, but forms with potassium iodide soluble salts, KHgI$_3$, K$_2$HgI$_4$; stannic sulphide forms a soluble sulphostannate, Na$_2$(SnS$_3$), (p. 52). Many oxalates, insoluble in water, form soluble complex salts with alkali oxalates, etc., — ferric, ferrous, cupric oxalates, etc., are instances. Students, in using the table, must, therefore, not neglect to consider the dependence of the solubility of a compound on other components which may be present.

SOLUBILITIES.[1]

Cobalt.	Nickel.	Zinc.	Manganese.	Silver.	Lead.	Mercurous.	Mercuric.	Cupric$_{13}$.	Bismuth.	Cadmium.	Arsenious.	Stannous.	Stannic.	Antimonous.	
A	A	A	A	A	A	A	A	A	A	A	A	A	A & I	A	1
A	A	A	A	......	A	......	....	A	A	A	......	A	A	A	2
W	W	W	W	I	W-I	A-I	W	W	W-A$_{15}$	W	W-A	W	W	W-A$_{17}$	3
W	W	W	W	I	W-I	A-I	W	W	w-a	W	W-A	w	w-a	w-a	4
W	W	W	W	I	W-I	A	A	W	a	W	w-a	W	w	w-a	5
a-i	a-i	A	a	I	a	......	W	a	....	a	......	....	......	....	6
I	I	A-I	a	I	a	......	....	I	i	a-i	......	i	i	....	7
I	I	A	I	I	w-a	......	i	....	i	a-i	......	i	......	....	8
w	w	w	w	I	a	A	W	a	....	w-a	......	....	w	....	9
A	A	A	A	A	A	A	A$_{12}$	A	A	A	A	A	A	A	10
W	W	W	W	W-A	A-I	W-A	W	W	w	W	......	W	......	....	11
A	A	A	A	A	A	a	a	A	A	A	......	....	......	....	12
a	a	a	a	A	A	a	a	A	....	......	......	....	......	a	13
a	a	a	a	a	A	a	a	a	a	a	......	....	......	a	14
a	a	w	w$_{\bullet}$	a	A-I	a	w-a	w	a	a	......	a	......	a	15
A	A	A	A	a	A	a	a	A	a	a	......	a	A	w-a	16
a	a	a	a	a	a	......	....	a	a	w-a	......	a	......	....	17
w-a	w-a	w-a	a	w	a	w	w-a	a	w	w-a	......	w	w	w	18
a	a	a	a	......	a	......	....	a	....	a	......	....	......	....	19
W	W	W	W	W	W	W	W	W	W-A$_{16}$	W	......	....	......	....	20
W	W	W	W	W	W	w	w	W	w	w	......	w	......	....	21
W	W	W	W	W	W	w-a	w	W$_{14}$	w	W	......	w	w	....	22
a	a	a	w-a	a	a	a	a	a	a	a	......	a	w	a	23
W	a	a	w-a	a	a	w-a	a	w	w	w-a	......	a	......	a$_{18}$	24

[1] The table is based, with a few modifications, on the table in Fresenius (Wells' Translation).

The solubilities, given in the table, refer to normal salts.[1] *Basic* salts (such as (BiO)Cl, (BiO)NO$_3$, etc.) are usually *less* soluble, *acid* salts *more* soluble, than are the normal salts.

---

[1] The ferric and chromic carbonates referred to in the table are *basic* carbonates.

A few of the more common salts, other than the normal salts, are given in the following list, together with comments on special cases, referred to in the table by subindices:

(1) Carbonic acid is only moderately soluble in water.

(2) Silicic acid may remain in colloidal " solution " in water.

(3) The acid salts, $KH(C_4H_4O_6)$ and $(NH_4)H(C_4H_4O_6)$, are somewhat difficultly soluble in water.

(4) Magnesium hydrosulphide, $Mg(SH)_2$, is soluble in water.

(5) The double salt, $Mg(NH_4)PO_4$, aq., is soluble in acids.

(6) Calcium sulphide is insoluble in, but decomposed by, water. The hydrosulphide is soluble.

(7) Calcium acid carbonate is soluble in water, but unstable.

(8) Calcium acid phosphate, $Ca(H_2PO_4)_2$, is soluble in water.

(9) Native, and strongly heated, aluminium oxide is insoluble in acids.

(10) Strongly heated chromium oxide is insoluble in acids.

(11) See Smith, p. 729, in regard to the chromium chlorides.

(12) Mercuric sulphide is soluble only in aqua regia.

(13) *Cuprous* salts are oxidized by the air, and more readily by hot nitric acid, to cupric salts. The chloride, bromide, iodide and sulphide are the most common and are very difficultly soluble or insoluble in water, but soluble in hot nitric acid as cupric salts.

(14) The basic acetate of copper: W–A.

(15) The basic chloride of bismuth or bismuth " oxychloride," (BiO)Cl, is soluble in acids.

(16) The basic or " sub " nitrate of bismuth is soluble in acids.

(17) The basic chloride of antimony or " algaroth powder " is soluble in acids.

(18) Potassium antimonyl tartrate, or " tartar emetic," $K(SbO)C_4H_4O_6$, is soluble in water.

TABLE OF EXACT SOLUBILITIES IN WATER

Under C the solubility is given in *gram molecules*, or *moles*, *per liter*, and under Gram/Liter, in *grams per liter*. Wherever reliable data were available, the values given represent the solubilities of the *non-hydrolyzed* salts (*e.g.* of the carbonates and sulphides, the total solubilities of whose hydrolyzed salts would be considerably greater than represented in the table). The degree of ionization is given under 100 α; for extremely dilute solutions it is assumed to be 100 per cent; for other solutions it is calculated from the conductivity relation $\alpha = \Lambda/\Lambda_0$ (Chap. IV), with the aid of data given in the articles referred to below or in related papers. The temperature to which the solubility refers is given with the author's name in the note to which each index refers.

If the table is used to calculate solubility-product constants, careful attention must be given to those salts from one molecule of which more than one ion of a given kind is obtained. Thus for Ag_2CrO_4 we have $Ag_2CrO_4 \rightleftarrows 2\,Ag^+ + CrO_4^=$. Since the total molar concentration is 0.0_48, $[CrO_4^=] = 0.0_48$ and $[Ag^+] = 2 \times 0.0_48 = 0.0_316$, the salt being assumed to be completely ionized at the concentration in question. Where the degree of ionization is less than 100 per cent, care must be taken to make allowance for it in the calculation; thus, for calcium sulphate (gypsum) the total concentration is 0.015 mole, but only 52.5 per cent of the salt is ionized: then $[Ca^{++}] = [SO_4^=] = 0.525 \times 0.015 = 0.0_279$.

Substance.	C	100 α	Gram/Liter.	Substance.	C	100 α	Gram/Liter.
K_2PtCl_6[9]	(0.023)	.....	11.2	MgF_2[1]	0.0_214	86	0.0874
$BaSO_4$[1]	0.0_41	98	0.0_223	$Ag(C_2H_3O_2)$[7]	0.059	72	9.90
$SrSO_4$[1]	0.0_362	84	0.114	$AgCl$[1]	0.0_594	100	0.0_2134
$CaSO_4$[1]	0.015	52.5	2.023	$AgBr$[1]	0.0_658	100	0.0_311
$BaCrO_4$[1]	0.0_414	89	0.0_235	AgI[1]	0.0_716	100	0.0_538
$SrCrO_4$[2]	0.0_26	.....	1.2	$AgSCN$[8]	0.0_511	100	0.0_318
$CaCrO_4$[2]	0.03	.....	4.0	$Ag(CN)$[3]	0.0_516	100	0.0_32
$BaCO_3$[6]	0.0_49	.....	0.018	$Ag[Ag(CN)_2]$[3]	0.0_515	100	0.0_34
$SrCO_3$[6]	0.0_445	.....	0.0_266	Ag_2O[3]	0.0_49	67	0.0214
$CaCO_3$[5]	0.0_311	.....	0.011	Ag_2CrO_4[1]	0.0_48	97	0.0252
$MgCO_3$[4]	0.0_25?	.....	0.42	Ag_3PO_4[3]	0.0_415	98	0.0_264
BaC_2O_4[1]	0.0_34	86	0.0905	Ag_2S[8]	$0.0_{16}22$	100	$0.0_{14}55$
SrC_2O_4[1]	0.0_326	89	0.046	$PbCl_2$[3]	0.035	.....	0.96
CaC_2O_4[1]	0.0_444	96	0.0_255	$PbBr_2$[3]	0.023	.....	0.83
MgC_2O_4[1]	0.0_227	33?	0.302	PbI_2[3]	0.0_213	97	0.047
$Ba(OH)_2$[2]	0.22	.....	37.0	$PbSO_4$[1]	0.0_313	92	0.041
$Sr(OH)_2$[2]	0.063	.....	7.7	$PbCrO_4$[1]	0.0_64	100	0.0_326
$Ca(OH)_2$[2]	0.02	.....	1.7	$Pb_3(PO_4)_2$[3]	0.0_617	100	0.0_313
$Mg(OH)_2$[2]	0.0_315	.....	0.0_29	PbS[8]	0.0_751	100	0.0_412
BaF_2[1]	0.0_291	82	1.60	HgI_2[1]	(0.0_68)	.....	(0.0_34)
SrF_2[1]	0.0_393	97	0.117	HgS[8]	$0.0_{26}17$	100	$0.0_{24}4$
CaF_2[1]	0.0_322	99	0.0163	CuS[8]	$0.0_{20}11$	100	$0.0_{18}1$

---

[1] Kohlrausch, *Z. phys. Chem.*, **64**, 168 (1908); the solubilities refer to 18°. [2] Kohlrausch und Holborn, *Leitfähigkeiten der Elektrolyte*, p. 202 (1898), and, in part, Kohlrausch und Rose, *Z. phys. Chem.*, **12**, 234 (1893), 18°. [3] Böttger, *Z. phys. Chem.*, **46**, 602 (1903), 20°. [4] Bodländer, *ibid.*, **35**, 23 (1900), 12°. [5] Stieglitz, *Publications of the Carnegie Institution*, No. 107, p. 248 (1908), at 16°; calculated by Bodländer's method from Schlösing's results. McCoy and H. J. Smith, *J. Am. Chem. Soc.*, **33**, 468 (1911), finds $C = 0.0_3104$, at 25°. [6] McCoy, *ibid.*, at 25°. [7] Arrhenius, *Z. phys. Chem.*, **31**, 221 (1899), 18.6°. [8] Knox, *Trans. Faraday Soc.*, **4**, 48 (1908), at 25°. [9] Treadwell, *Qualitative Analysis* (1902), 20°.

REAGENTS AND SOLUTIONS

The solutions of reagents used in systematic analysis are, as a rule, made rather concentrated, so that often only a small quantity of the reagent is needed, sometimes only a *few drops*, if a small volume of solution is being tested. The solutions of substances used for the study of reactions, are more dilute, as a rule, and, in general, are of *one-tenth molar* concentration. Stronger solutions may be kept in stock if desired.

The solutions are prepared, in general, simply by the solution of the weight, indicated by the formula (including the water of crystallization represented by " aq.") and by the molar concentration, in sufficient water to give one liter of solution. Where a different method of preparation is required, special instructions are given.

Desk Reagents

Acetic Acid, $C_2H_4O_2$, 6 M.
Ammonium Carbonate, $(NH_4)_2CO_3$, M. (157 grams of "ammonium carbonate" [$(NH_4)HCO_3$, $NH_4CO_2NH_2$] are dissolved in 75 c.c. of conc. ammonium hydroxide (sp. gr., 0.90) and sufficient water to make a liter.)
Ammonium Chloride, NH_4Cl, 4 M.
Ammonium Hydroxide, NH_4OH, NH_3, 6 M.
Ammonium Oxalate, $(NH_4)_2C_2O_4$, aq. M/4.
Ammonium Phosphate, $(NH_4)_2HPO_4$, M.
Ammonium Sulphide, $(NH_4)_2S$, [NH_4SH, NH_4OH]. (300 c.c. of 6-molar NH_4OH is saturated with H_2S; 200 c.c. of 6-molar ammonium hydroxide and sufficient water are added to the mixture to make a liter.)
Ammonium Sulphide, yellow, $(NH_4)_2S$, etc., *and* $(NH_4)_2S_x$. (The previous solution is digested with flowers of sulphur, 1 to 2 grams to the liter.)
Barium Chloride, $BaCl_2$, 2 aq. M.
Calcium Hydroxide, $Ca(OH)_2$ (" limewater ") saturated, M/50.
Hydrochloric Acid, HCl, 6 M. (Sp. gr., 1.1; 465 c.c. conc. HCl (sp. gr., 1.2) in 1 liter.)
Hydrochloric Acid, Conc., 13 M. (Sp. gr., 1.20.)
Lead Acetate, $Pb(C_2H_3O_2)_2$, 3 aq. M.
Nitric Acid, 6 M. (Sp. gr., 1.195; 382 c.c. conc. acid (sp. gr., 1.42) in 1 liter.)
Nitric Acid, Conc., 16 M. (Sp. gr., 1.42.)
Potassium Dichromate, $K_2Cr_2O_7$, M/4.
Silver Nitrate, $AgNO_3$, M/4.
Sodium Carbonate, Na_2CO_3, M.
Sodium Hydroxide, NaOH, 2 M.
Sulphuric Acid, H_2SO_4, 3 M. (Sp. gr., 1.18; 167 c.c. conc. acid in 1 liter.)

Side-Shelf Liquid Reagents and Solutions

Acetic Acid, $C_2H_4O_2$. (5 per cent.)
Alcohol, C_2H_6O. (95 per cent.)
Aluminium Nitrate, $Al(NO_3)$, 7.5 aq. M/10.
Aluminium Sulphate, $Al_2(SO_4)_3$, 18 aq. M/10.
Ammonium Carbonate, $(NH_4)_2CO_3$; (according to Bray; see p. **20**).
Ammonium Chloride, NH_4Cl, M.
Ammonium Hydroxide, M; and conc., 15 M. (Sp. gr., 0.90.)
Ammonium Molybdate Solution, *Nitric Acid Solution.* A solution of ammonium nitrate and of molybdic acid in nitric acid, containing probably more or less *hydrolyzed* molybdic nitrate, $MoO_2(NO_3)_2$. (150 grams of

ammonium molybdate $(NH_4)_6Mo_7O_{24}$, 4 aq. are dissolved in water to make 1 liter and this solution is added to a liter of 6-molar nitric acid (sp. gr., 1.2).[1] The addition of ammonium nitrate (15 grams per 100 c.c. solution) increases the sensitiveness of the reagent).

Ammonium Molybdate Solution, *without nitric acid.*[2] *Before using this solution, mix some of it with an equal volume of nitric acid* (dilute nitric acid, 6-molar, of the desk reagents); the addition of 1 or 2 grams of ammonium nitrate, per 10 c.c. of the acidified mixture, increases the sensitiveness of the reagent. (150 grams of ammonium molybdate in 1 liter.)

Ammonium Nitrate, NH_4NO_3, 4 M.

Ammonium Thiocyanate (Sulphocyanate), NH_4SCN, M.

Antimony Trichloride, $SbCl_3$, M/10. (The solution is prepared with the aid of hydrochloric acid.)

Arsenious Acid, $HAsO_2$, M/10. (10 grams As_2O_3 in 1 liter.)

Barium Carbonate, Suspension or Milk of. Shake the mixture well and use the suspension, not the solution. ($BaCO_3$ is finely ground with water to form a thick milk.)

Barium Chloride, $BaCl_2$, 2 aq. M; M/10; and a saturated solution.

Barium Hydroxide, $Ba(OH)_2$, 8 aq. M/6.

Barium Nitrate, $Ba(NO_3)_2$, M/2.

Benzene, C_6H_6.

Bismuth Nitrate, $Bi(NO_3)_3$, M/10. (Prepared with the addition of nitric acid.)

Bromine Water, saturated.

Cadmium Nitrate, $Cd(NO_3)_2$, 4 aq. M/10.

Cadmium Sulphate, $CdSO_4$, 4 aq. M/10.

Calcium Chloride, $CaCl_2$, 6 aq. M; M/10.

Calcium Nitrate, $Ca(NO_3)_2$, 4 aq. M.

Calcium Sulphate, $CaSO_4$, 2 aq. sat. sol., 0.015 M.

Carbon Disulphide, CS_2.

Chlorine Water, sat. sol. (Keep in black bottles.)

Chloroform, $CHCl_3$.

Chloroplatinic Acid, H_2PtCl_6, 6 H_2O, M/5. (Kept in the storeroom.)

Chromium Nitrate, $Cr(NO_3)_3$, 9 aq. M/10.

Chrome-Alum, $KCr(SO_4)_2$, M/10.

Cobalt Chloride, $CoCl_2$, 6 aq. M/10.

Cobalt Sulphate, $CoSO_4$, 7 aq. M/10.

Cupric Nitrate, $Cu(NO_3)_2$, 6 aq. M/10.

Cupric Sulphate, $CuSO_4$, 5 aq. M/10.

Ether, $C_4H_{10}O$.

Ether-alcohol. (A mixture of equal volumes of anhydrous ether and anhydrous alcohol.)

Ferric Chloride, $FeCl_3$, 6 aq. M/10.

---

[1] Treadwell's *Qualitative Analyse*, p. 174 (1902).

[2] This solution keeps very much better than the nitric acid solution, but is less convenient to use.

Ferric Sulphate, $Fe_2(SO_4)_3$, 9 aq. M. (The solution may also be prepared as follows:[1] 50 grams $FeSO_4$, 7 aq., 40 c.c. 3-molar H_2SO_4 and 3 c.c. conc. HNO_3 are mixed and the mixture heated rapidly to boiling and boiled vigorously to expel nitric oxide. The solution is diluted to 250 c.c.)

Gold Chloride, $AuCl_3$, 2 aq. M/500. (Kept in the storeroom.)

Hydrochloric Acid, M, M/4, M/10.

Hydrofluoric Acid, H_2F_2. (Kept in the storeroom.)

Lead Nitrate, $Pb(NO_3)_2$, M/10.

Magnesium Chloride, $MgCl_2$, 6 aq. M; M/10.

Magnesium Nitrate Mixture:[2] $Mg(NO_3)_2$, NH_4NO_3, NH_4OH. (65 grams of magnesium nitrate, $[Mg(NO_3)_2$, 6 aq.], 200 grams of ammonium nitrate and 100 c.c. of conc. ammonium hydroxide are dissolved to 1 liter in water.)

Magnesium Sulphate, $MgSO_4$, 7 aq. M; M/5.

Manganous Chloride, $MnCl_2$, 4 aq. M/10.

Mercuric Chloride, $HgCl_2$, M/10.

Mercuric Cyanide, $Hg(CN)_2$, M/10.

Mercuric Nitrate, $Hg(NO_3)_2$, M/10.

Mercurous Nitrate, $Hg(NO_3)$, M/10.

Methyl Alcohol, CH_4O. (Wood alcohol.)

Methyl Orange, $(CH_3)_2N.C_6H_4N_2C_6H_4SO_3Na$. (One gram in 1 liter.)

Methyl Violet, $[(CH_3)_2N.C_6H_4]_2C[C_6H_4N(CH_3)_2Cl]$. (1 part in 12,500 parts of water.)

Nickelous Chloride, $NiCl_2$, 6 aq. M/10.

Nickelous Sulphate, $NiSO_4$, 6 aq. M/10.

Phenolphthalein, $(HOC_6H_4)_2C(C_6H_4CO_2)$. (5 grams in a liter of 50 per cent alcohol.)

Potassium Arseniate, K_2HAsO_4, M/10.

Potassium Arsenite, K_2HAsO_3, M/10.

Potassium Bromide, KBr, M; M/10.

Potassium Chloride, KCl, M; M/10.

Potassium Chromate, K_2CrO_4, M.

Potassium Cyanide, KCN, M.

Potassium Hydroxide, KOH, 2 M.

Potassium Iodide, KI, M; M/10.

Potassium Nitrite, KNO_2, M/10; M/1000.

Potassium Pyroantimonate, $K_2H_2Sb_2O_7$. (2 grams of $K_2H_2Sb_2O_7$ are added to 100 c.c. of boiling water, the mixture is boiled until the salt is dissolved, and the solution cooled quickly. 3 c.c. of 10 per cent KOH solution is added to it to render the reagent alkaline.)[3]

Silver Sulphate, Ag_2SO_4, M/50. Saturated solution.

---

[1] W. A. Noyes, *Qualitative Analysis*, p. 98 (1905).

[2] For qualitative analysis the nitrate mixture is preferable to the chloride mixture, generally recommended, because the test with the reagent for phosphate or arseniate ions may then be more conveniently followed by the test in which the magnesium salt is converted into a silver salt.

[3] Bray, *J. Am. Chem. Soc.*, **31**, 623 (1909).

Sodium Acetate, $NaC_2H_3O_2$, 3 aq. M.

Sodium Benzoate, $NaC_7H_5O_2$, aq. M.

Sodium Chloride, NaCl, M; M/10.

Sodium Cobaltinitrite, $Na_3Co(NO_2)_6$. (100 grams of $NaNO_2$ are dissolved in 200 c.c. of water, and to this solution 50 c.c. of 6-molar acetic acid and 10 grams of $Co(NO_3)_2$, 6 aq., are added. After a day or two the solution is filtered from any precipitate, $K_2Na[Co(NO_2)_6]$, aq., and diluted to 400 c.c.)[1]

Sodium Hydroxide, NaOH, conc. solution (about 10 M). (A solution that is tolerably free from carbonate, is obtained by allowing the carbonate to settle out of a saturated solution of the hydroxide. The solution is decanted, and diluted with an equal volume of water.)

Sodium Oxalate Reagent (according to Bray; see p. 21).

Sodium Phosphate, Na_2HPO, 12 aq. M/2; M/10.

Sodium Potassium Tartrate (Rochelle Salt), $NaKC_4H_6O_6$, 4 aq. M.

Sodium Salicylate, $NaC_7H_5O_3$, M.

Sodium Sulphostannate, Na_2SnS_3, M/4. (45 grams of SnS_2 are dissolved in a concentrated solution of 60 grams of Na_2S; the solution is diluted to 1 liter.)

Stannous Chloride, $SnCl_2$, 2 aq. M/10. (The solution is prepared with the addition of hydrochloric acid and some pure tin.)

Starch Solution. (A solution of 1 gram of "soluble starch" in 250 c.c. of water is prepared, and 1 c.c. of chloroform added to the solution to preserve it. Or, 1 gram of arrowroot starch is rubbed with 10 c.c. of cold water and the suspension poured into 150 c.c. of boiling water. Boil the mixture half a minute, dilute it with 350 c.c. of water and add 2 c.c. of chloroform to the cold solution.)

Strontium Chloride, $SrCl_2$, 6 aq. M; M/10.

Strontium Sulphate, $SrSO_4$, 0.0006 molar. Saturated solution.

Sulphanilic Acid-Naphthylamine Reagent (Griess-Ilvosay Reagent). ***Equal volumes of the separate solutions are mixed to prepare the reagent just before it is used.*** (A gram of sulphanilic acid, $H_2NC_6H_4SO_3H$, is dissolved in 14.7 grams of warm glacial acetic acid and an equal volume of water. Then more water is added until 285 c.c. have been used altogether. Similarly 0.2 gram of α-naphthylamine, $C_{10}H_7NH_2$, is dissolved in 14.7 grams of glacial acetic acid and two volumes of water, and water is then added until 325 c.c. have been used.)

Sulphuric Acid, Conc., 18 M. (Sp. gr., 1.84.)

Zinc Chloride, $ZnCl_2$, M/10.

Zinc Sulphate, $ZnSO_4$, 7 aq. M/10.

SOLIDS

Absorbent Cotton.
Aluminium Sulphate, $Al_2(SO_4)_3$, 18 aq.
Ammonium Acetate, $NH_4C_2H_3O_2$.
Ammonium Chloride, NH_4Cl.
Ammonium Fluoride, $(NH_4)_2F_2$.
Ammonium Nitrate, NH_4NO_3.
Ammonium Sulphate, $(NH_4)_2SO_4$.
Antimony Pentoxide, Sb_2O_5.
Antimony Trioxide, Sb_2O_3.
Arsenic Sulphide, As_2S_3.
Arsenic Trioxide (Arsenious "Acid") As_2O_3.

---

[1] Bray, *loc. cit.*

Barium Carbonate, $BaCO_3$.
Barium Hydroxide, $Ba(OH)_2$, 8 aq.
Barium Peroxide, $Ba(O_2)$.
Barium Sulphate, $BaSO_4$.
Benzoic Acid, $C_7H_6O_2$.
Bismuth Nitrate, $Bi(NC_3)_3$.
Boric Acid, H_3BO_3.
Cadmium Sulphate, $CdSO_4$, 4 aq.
Calcium Carbonate, $CaCO_3$.
Calcium Fluoride (Fluorspar), CaF_2.
Calcium Oxide, CaO.
Calcium Phosphate, $Ca_3(PO_4)_2$.
Chloride of Lime (Bleaching Powder), Ca(OCl)Cl.
Chrome-Alum, $KCr(SO_4)_2$, 12 aq.
Cobalt Nitrate, $Co(NO_3)_2$, 6 aq.
Copper Wire.
Cupric Oxide, CuO, powdered.
Ferric Oxide, Fe_2O_3.
Ferrous Sulphate, $FeSO_4$, 7 aq.
Ferrous Ammonium Sulphate, $FeSO_4$, $(NH_4)_2SO_4$, 6 aq.
Ferrous Sulphide, FeS.
Iodine.
Iron Filings.
Iron Nails.
Lead Dioxide, PbO_2. (Manganese free.)
Lead Dioxide, PbO_2. (Purified.)
Lead Nitrate, $Pb(NO_3)_2$.
Lead Sulphide, PbS.
Litmus Paper, red. (*Slightly* acid.)
Litmus Paper, violet. (Neutral.)
Logwood Chips.
Magnesium Oxide, MgO.
Manganese Dioxide, MnO_2. (Precipitated.)
Manganese Sulphate, $MnSO_4$, 7 aq.
Mercuric Nitrate, $Hg(NO_3)_2$.
Mercuric Sulphide, HgS.
Mercurous Nitrate, $Hg(NO_3)$.
Nickelous Chloride, $NiCl_2$, 6 aq.
Paraffine.
Potassium Bromide, KBr.
Potassium Carbonate, K_2CO_3.
Potassium Chlorate, $KClO_3$.
Potassium Chloride, KCl.
Potassium Cyanide, KCN.
Potassium Dichromate, $K_2Cr_2O_7$.
Potassium Ferricyanide, $K_3Fe(Cn)_6$.
Potassium Ferrocyanide, $K_4Fe(CN)_6$, 3 aq.
Potassium Hydrogen Sulphate, $KHSO_4$. (Fused.)
Potassium Iodide, KI.
Potassium Nitrate, KNO_3.
Potassium Nitrite, KNO_2.
Potassium Oxalate, $K_2C_2O_4$.
Potassium Permanganate, $KMnO_4$.
Potassium Sulphate, K_2SO_4.
Potassium Thiocyanate, KSCN.
Salicylic Acid, $C_7H_6O_3$.
Sand, Sea.
Silicon Dioxide (Silica), SiO_2.
Soda-lime, $Ca(OH)_2$, NaOH.
Sodium Acetate, $NaC_2H_3O_2$, 3 aq.
Sodium Ammonium Phosphate (*Microcosmic Salt*), $NaNH_4HPO_4$, 4 aq.
Sodium Benzoate, $(C_7H_5O_2)Na$, aq.
Sodium Carbonate, Na_2CO_3.
Sodium Chloride, NaCl.
Sodium Hydroxide, NaOH. (Purified.)
Sodium Nitrate, $NaNO_3$.
Sodium Nitroprussiate, $Na_2Fe(CN)_5(NO)$, 2 aq.
Sodium Peroxide, $Na_2(O_2)$.
Sodium Acid Phosphate (monobasic), NaH_2PO_4, 4 aq.
Sodium Phosphate (dibasic), Na_2HPO_4, 12 aq.
Sodium Phosphate (tribasic), Na_3PO_4, 12 aq.
Sodium Potassium Tartrate (Rochelle Salt), $NaKC_4H_4O_6$, 4 aq.
Sodium Silicate, Na_2SiO_3.
Sodium Stannate, Na_2SnO_3, 3 aq.
Sodium Sulphide, Na_2S, 9 aq.
Sodium Tetraborate (Borax), $Na_2B_4O_7$, 10 aq.
Starch, $(C_6H_{10}O_5)_x$.
Strontium Chloride, $SrCl_2$, 6 aq.
Sulphur, S.
Tartaric Acid, $C_4H_6O_6$.
Tin (foil).
Tin (granulated).
Turmeric Paper.
Zinc (dust).
Zinc (granulated).
Zinc Sulphate, $ZnSO_4$, 7 aq.

ADDENDA

THE DETECTION OF NICKEL IN THE PRESENCE OF COBALT, AND OF CADMIUM IN THE PRESENCE OF COPPER, WITHOUT THE USE OF POTASSIUM CYANIDE.

For teachers who wish to avoid having their pupils handle potassium cyanide, the following methods of separating nickel from cobalt, and cadmium from copper, are recommended. For more mature and professional students the cyanide methods of separation are recommended as more sensitive and more convenient.

Additions to the Reactions of Nickel and Cobalt, Vol. II, p. 33.

5. (*a*) To 1 c.c. of nickel sulphate solution add enough ammonia to redissolve the precipitate first formed and then add 1 or 2 c.c. in excess. To the resulting solution add 10 c.c. of a 10 per cent cane-sugar solution and then about 0.1 gram of dicyandiamidine (guanylurea) sulphate[1] (storeroom). Stir the mixture to hasten the solution and then add enough sodium hydroxide solution to produce a decided color change. Stir the mixture vigorously with a glass rod and scratch the sides of the vessel to promote crystallization. The precipitate is nickel dicyandiamidine, Ni $(C_2H_5N_4O)_2$, 2 aq.

(*b*) Treat as above 1 c.c. of cobalt sulphate solution. The violet color is a test for cobalt but not as sensitive a one as the nitrite test (§ 4 (*c*), p. 33).

Additions to the Analysis of the Aluminum and Zinc Groups, Determination of Cobalt and Nickel, Vol. II, p. 36.

Treat the whole of the residue (**R**) exactly as described in the text to the sign (X) in the last line of p. 36. From this point on proceed as follows (*do not use potassium cyanide*): Divide the solution into two equal parts.[2] One of these is tested for **cobalt** as in § 3, p. 37. The other portion is tested as in 5 (*c*) above for **nickel** with Grossmann's reagent. If no precipitate is formed when the mixture is vigorously stirred, add 0.1 to 0.2 gram more of the reagent and allow the mixture to stand overnight. Any precipitate is collected, washed well with water to remove cobalt, and tested with the borax bead to confirm **nickel.**

Additions to the Reactions of Copper and Cadmium, Vol. II, p. 46.

Add to § 1, under copper, p. 46 (*do not try the cyanide test*), the following:

(*e*) Add an excess of ammonia solution to some copper sulphate solution and then to a small portion of the resulting solution add ammonium sulphide.

(*f*) Just neutralize, with sulphuric acid, the remainder of the ammoniacal solution prepared in (*e*), add a drop of acid in excess and then some iron filings. Allow the reaction to continue until a drop of the solution is found free from copper; then filter the mixture, add a few drops of sulphuric acid to it and pass hydrogen sulphide into it.

Add the following to § 1 under Cadmium, p. 46 (*do not try the cyanide test*):

(*e*) To a solution of cadmium sulphate add a drop of sulphuric acid and then some iron filings. After a little while, filter the solution and pass hydrogen sulphide into it.

(*f*) Treat as in § 1 (*f*) under copper (see above) a mixture of copper and cadmium sulphate solutions. After Chapters XIV and XV, Vol. I, have been studied, explain your results (see the table, p. 294).

Addition to the Analysis of the Copper Group, Vol. II, p. 51.

Substitute for § 4 (*do not use potassium cyanide*) the separation of cadmium and copper by means of iron filings[3] as given above under cadmium, 1 (*f*). Before passing hydrogen sulphide into the solution test the latter with methyl violet and adjust the hydrogen ion concentration until it gives the blue green tint with the indicator. If the color of the precipitate obtained with hydrogen sulphide makes the presence of cadmium doubtful, it is collected and examined further according to the last few lines of § 4, p. 51.

---

[1] Grossmann's nickel reagent, *cf. Ber. d. chem. Ges.*, **39**, 3356 (1906) and **41**, 1879 (1908).

[2] The whole solution may also be treated according to § 3, p. 37, and **cobalt** be completely precipitated as $K_3Co(NO_2)_6$, the mixture being allowed to stand in a warm place at least several hours. **Nickel** may then be found in the filtrate from the $K_3Co(NO_2)_6$ by precipitation as $Ni(OH)_2$ with sodium hydroxide, and confirmed by the borax bead or dicyandiamidine test.

[3] *Cf.* W. A. Noyes, Qualitative Analysis, 1911, p. 32.

Chlorides: detection, *see* chloride group
  identification, 72, 74, 75, 125
  reactions, 72
Chromates: detection, 116, 118
  reactions, 67
Chromites, 25, 67
Chromium: detection, *see* aluminium group and chromates
  identification, 38
  reactions, 25
Cobalt: detection, *see* zinc group
  identification, 36, 37
  reactions, 32
Complex ions, 29, 43, 44, 46, 59, 71, 83
Copper: detection, *see* copper group
  identification, 51
  reactions, 46
Copper group: analysis, 48, 49
  characteristics, 48
  detection, 100–104, 135–139
  reactions, 41
Cuprous salts, 142
Cyanides, complex ions of, 29, 33, 43, 46, 88
  detection, *see* chloride group
  identification, 125
  modifying course of analysis, 88
  precautions against, 33, 75, 88
  reactions, 75

Ferric-ion, *see* iron
Ferricyanides: detection, 88, 125
  reactions, 29, 76
Ferrocyanides: detection, 88, 125
  reactions, 29, 76
Ferrous-ion, *see* iron
Flame spectra, 7
Flame tests, 5, 15, 91
Fluorides: detection, 92, 128, 134
  precautions due to, 88, 135, 137
  reactions, 76
Fluorosilicates, 71, 124
Fractional precipitation, 15, 17, 68

Gold: detection, *see* arsenic group
  identification, 106
  reactions, 58

Hydrochloric acid, as solvent, 94, 96
Hydrocyanic acid, precautions against, 33, 75, 88
Hydrogen-ion: detection, 93, 96
Hydrogen sulphide, precipitation by, 31, 41, 49, 61, 100
Hydrolysis, 23, 28, 47, 79
Hydroxide-ion: detection, 93, 96

Insoluble substances: analysis, 130
Iodides: detection, *see* chloride group
  identification, 73–75
  reactions, 72
Ion-product, *see* solubility-product
Iron:
  Ferric-ion: detection, *see* aluminium group
    identification, 37
    reactions, 27
  Ferrous-ion: detection, *see* aluminium and zinc groups
    identification, 38
    reactions, 32

Lead: detection, *see* silver group and copper group
  identification, 48
  reactions, 44
Liquids: analysis, 93

Magnesium: detection, *see* alkaline earth group
  identification, 18, 22
  reactions, 8
Manganese:
  Manganous-ion: detection, *see* zinc group
    identification, 40
    reactions, 34
  Permanganates, 68
Melting point, 84
Mercury:
  Mercuric-ion: detection, *see* copper group
    identification, 50
    reactions, 45
  Mercurous-ion: detection, *see* silver group
    identification, 49
    reactions, 45
Metal ions: systematic analysis, 100, 130
Metals, 92, 98
Metaphosphate bead, 26, 91
Methyl violet, 31, 49, 61, 102

Nickel: detection, *see* zinc group
  identification, 37
  reactions, 32
Nitrate group, 67
  analysis, 128
  reactions, 79
Nitrates: detection, 128, 136
  reactions, 79
Nitric acid, as solvent, 94, 97
Nitrites, 80, 119

ORGANIC acids, group of, 67
  detection, 81, 129
  reactions, 81
Organic substances: detection, 81, 87, 89, 90, 92
  modifying course of analysis, 87, 107, 115, 122
Oxalates, complex ions of, 140
  detection, 129
  reactions, 82
Oxidation, 25, 27, 56, 73, 82

PERMANGANATES, 68
Phosphate group, 66
  detection, 126
  reactions, 76
Phosphates: detection, 127, 136, 139
  modifying course of analysis, 108
  reactions, 77
Platinum: detection, *see* arsenic group
  identification, 105
  reactions, 58
Platinum ware, 138
Plumbites, 65
Potassium: detection, *see* alkali group
  identification, 115
  reactions, 3

REAGENTS, 143–149
Record, 88
Reduction, 27, 56, 57, 73

SALICYLATES: detection, 130
  reactions, 86
Silicates, analysis of, 134
  detection, 91, 111, 118, 135, 138
  modifying course of analysis, 88
  reactions, 69
Silver: complex ions, 42
  detection, *see* silver group
  identification, 49
  reactions, 42
Silver group: analysis, 48
  characteristics, 48
  detection, 100, 131, 132
  reactions, 41
Sodium: detection, *see* alkali group
  identification, 115
  reactions, 3
Solubilities, 141
  exact, 143
Solubility-product, 10, 17
Spark spectra, 12
Spectroscope, 5
Stannates, 56, 67, 116
Stannic-ion, 57
Stannites, 56, 67, 116
Stannous-ion, 57
Strontium: detection, *see* alkaline earth group
  identification, 19, 21
  reactions, 15
Sulphate group, 66
  reactions, 71
Sulphates: detection, 123, 133, 136, 139
  reactions, 71
Sulphides: detection, 93, 96, 119
  reactions, 71
Sulphocyanates, *see* thiocyanates
Sulphur, 131

TARTRATES: detection, 129
  reactions, 83
Thiocyanates: detection, 125
  reactions, 76
Tin: detection, *see* arsenic group, 131
  identification, 62, 107
  reactions, 56

WATER: detection, 89

ZINC: detection, *see* zinc group
  identification, 40
  reactions, 34
Zincates, 34, 116
Zinc group: analysis, 35
  characteristics, 35
  detection, 110, 113, 135, 139
  reactions, 30

LANE MEDICAL LIBRARY

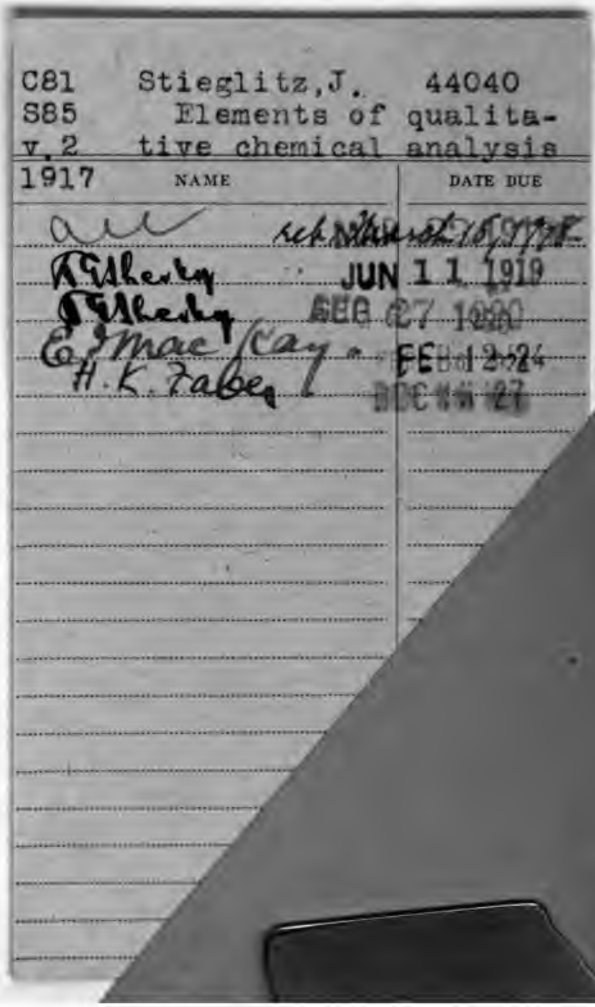
To avoid fine, this book should be returned on
or before the date last stamped below.

MAY 23 1919

AUG 27 1920

FEB 12 '24

DEC 13 '27

C81 Stieglitz, J. 44040
S85 Elements of qualitative chemical analysis
v. 2
1917

NAME	DATE DUE
	rcb March 16, 1918
F Etherly	JUN 11 1919
F Etherly	DEC 27 1920
E. J. MacKay	FEB 12 '24
H. K. Faber	DEC [illegible] '27